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THE UNIVERSITY OF ALBERTA

ORGANIC DEOXYGENATIONS WITH
SELENIUM AND TELLURIUM REAGENTS

by



STEVEN M. MENCHEN

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND
RESEARCH IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

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THE UNIVERSITY OF ALBERTA

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Research, for acceptance, a thesis entitled ORGANIC
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submitted by Steven M. Menchen in partial fulfilment
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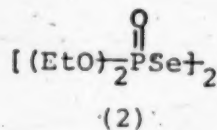
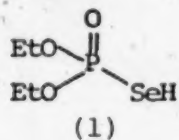
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ABSTRACT

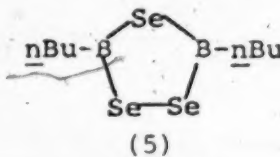
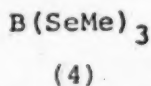
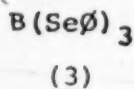
This thesis deals with three sections: the deoxygenation of sulfoxides using selenium-phosphorus and selenium-boron reagents; the preparation of selenoacetals using selenium-boron reagents; and the deoxygenation of epoxides by means of a tellurium-phosphorus reagent.

O,O-Diethyl hydrogenphosphoroselenoate (1) was found to reduce simple aliphatic sulfoxides efficiently into sulfides, the reduction requiring two moles of (1) per



mole of sulfoxide. The neat byproduct, bis(O,O-diethyl phosphoryl) diselenide (2) was found to slowly reduce dimethyl sulfoxide to dimethyl sulfide. The reductions with (1) were slow for hindered and aryl sulfoxides.

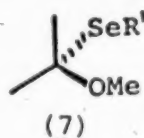
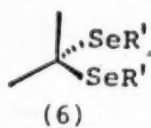
Tris(phenylseleno)borane (3), tris(methylseleno)borane (4), and 3,5-di-n-butyl-1,2,4,3,5-triselenodiborolane (5)



were all found to be very effective for the reduction of sulfoxides to sulfides. (3) gave high yields of diphenyl- and di-t-butyl sulfide from the respective sulfoxides, selectively reduced a β -keto sulfoxide to the β -keto

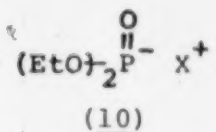
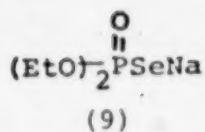
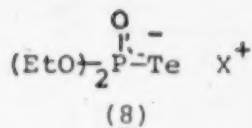
sulfide level, and gave a high yield of vinyl sulfide from a vinyl sulfoxide, although the latter occurred with loss of stereochemistry.

Selenoacetals (6) were prepared from (3) (for (6), $R' = \emptyset$) in the presence of a small amount (1 - 15%) of



trifluoroacetic acid (TFA) with aliphatic and aromatic ketones and aldehydes. Higher yields were obtained by a TFA-catalyzed acetal exchange reaction with the corresponding oxygen acetals; in the absence of TFA, high yields of the intermediate mixed oxygen-selenium acetals ((7), $R' = \emptyset$) were isolated and characterized. Excellent yields of selenoacetals ((6), $R' = \text{Me}$) were isolated from aliphatic and aromatic ketones with (4) and a small amount of TFA, but (4) was found to be inferior to (3) for the preparation of selenoacetals of an aliphatic aldehyde. An α, β -unsaturated ketone gave a low yield of unstable selenoacetal with (4).

Lithium O,O-diethyl phosphorotelluroate ((8), $X = \text{Li}$) in ethanol stereospecifically deoxygenated epoxides into olefins with retention of configuration. (8) was a much superior epoxide deoxygenation reagent to the analogous selenium reagent (9). The reagents are readily accessible



from the reaction of the phosphite (10) in ethanol or, preferably, THF; however, the deoxygenation does not occur in THF. The deoxygenation was found to be catalytic in tellurium when a tellurium-terminal epoxide mixture was treated with an ethanolic solution of (10); stoichiometric amounts of tellurium were required for internal epoxides. Of the three cations tested (potassium, sodium, lithium), lithium was superior. The deoxygenation was selective for terminal epoxides in the presence of internal epoxides, and selective for (Z)-epoxides in the presence of the (E)-isomers.

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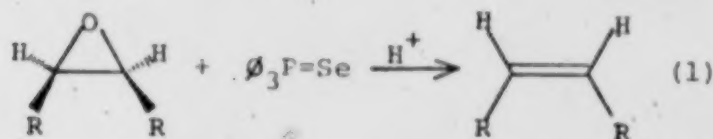
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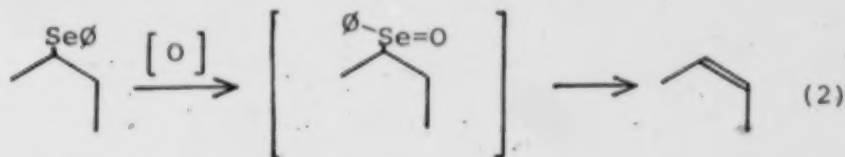
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The organic chemistry of selenium has been dominated by the use of selenium dioxide for allylic hydroxylation and alpha dione formation,^{1a,b} and the use of selenium metal for dehydrogenation and olefin isomerization. In 1973 it was discovered that triphenylphosphine selenide converts epoxides stereospecifically into olefins in the presence of acid² (eq. (1)),

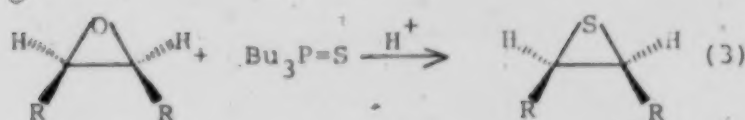


but the major use of selenium in organic synthesis has centered around the selenoxide fragmentation for the preparation of olefins³ (eq. (2)).



In retrospect, some of the recent developments of organic transformations using selenium could have come from direct analogy with known sulfur reaction mechanisms. The deoxygenation of epoxides using triphenylphosphine selenide was developed as a direct result of the observation that epoxides are stereospecifically converted into episulfides by treatment with a phosphine sulfide in the presence of acid⁴ together with the knowledge, from the spectroscopy literature, that episelenides

are very unstable. (eq. (3)). The syn elimination



of selenoxides was predictable from the well studied sulfoxide fragmentation,⁵ although the merit of the selenium processes was not recognized for many years. The current popularity of the selenium reagents arises from the facility of their reactions compared to the sulfur processes.

I would first like to discuss some relevant sulfur chemistry and its use for deoxygenating organic compounds before entering into the selenium and tellurium reagents.

Sulfur compounds have been widely used for organic deoxygenations, frequently by exchange of sulfur from another atom (X) that forms a strong bond to oxygen (eq. (4)). The most common atoms used with sulfur in



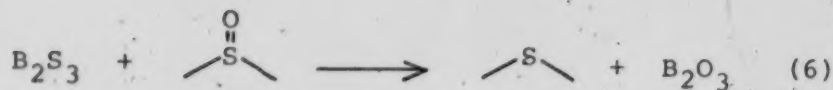
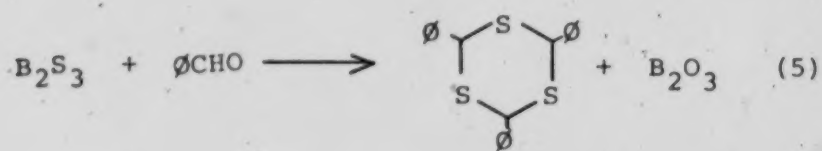
this context are boron, phosphorus, silicon and aluminum, which have the oxygen bond strengths shown in Table I. Carbon and hydrogen bond strengths with oxygen have been included for comparison.

Boron sulfur compounds are extremely unstable in the presence of moisture,⁸ but have found little use

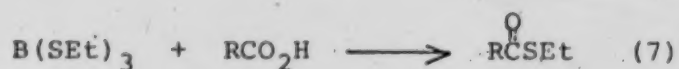
TABLE I. SOME OXYGEN BOND STRENGTHS

<u>Bond</u>	<u>Strength</u> (kcal/mole)
B-O (Boron esters)	125 ⁶
Si-O (SiO ₂)	111 ⁶
P-O (P ₄ O ₆)	88 ⁶
P=O	~140 ⁷
C-O (Organic)	85 ⁶
C=O (Ketones)	179 ⁶
Al-O	Not available
H-O (H ₂ O)	111 ⁶

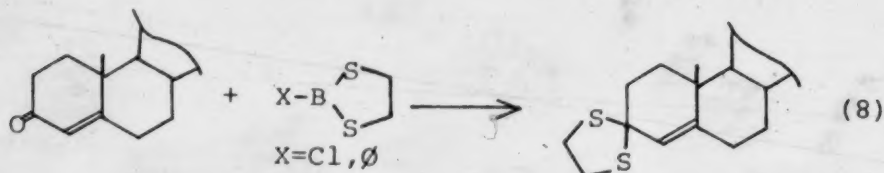
in organic synthesis. Boron sulfide has been shown to deoxygenate non-enolizable aldehydes to give trimerized thioaldehydes⁹ (eq. (5)) and to deoxygenate sulfoxides¹⁰ (eq. (6)). Alkylthioboranes react with



acids to give high yields of thioesters¹¹ (eq. (7)) and



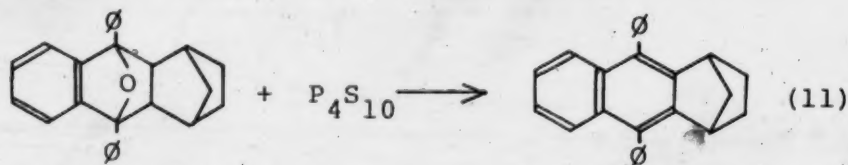
with aldehydes¹² and ketones¹³ to give good to excellent yields of thioacetals (eq. (8)).



The use of phosphorus-sulfur reagents for organic deoxygenation has been much more extensive. Phosphorus-pentasulfide has been used for the deoxygenation of acetamide^{14a} (eq. (9)), ketones and esters^{14b} (eq. (10)),



bicyclic ethers^{14c} (eq. (11)) and sulfoxides^{10,14d}

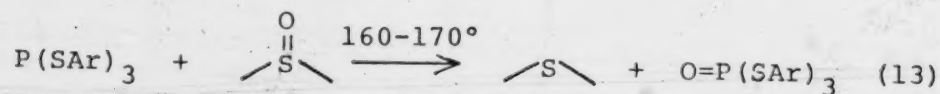


(eq. (12)). The use of trialkylphosphine sulfides for

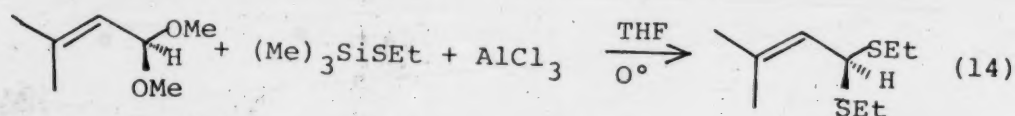


the deoxygenation of epoxides has been noted (eq. (3)). Trialkyl thiophosphites do not appear to be active deoxygenation reagents; the only example in the literature is for deoxygenation of dimethyl sulfoxide,¹⁵

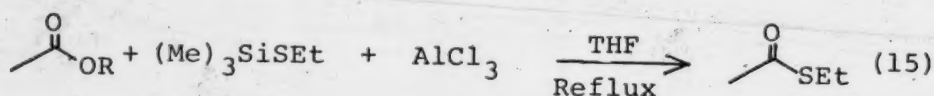
a reaction that requires high temperatures, and takes place without cleavage of a phosphorous-sulfur bond (eq. (13)).



It was not until 1974 that the ability of silicon-sulfur compounds to effect deoxygenations was shown by Mukaiyama, using trimethylsilyl ethylthiolate to deoxygenate α,β -unsaturated acetals^{16a} (eq. (14)), and

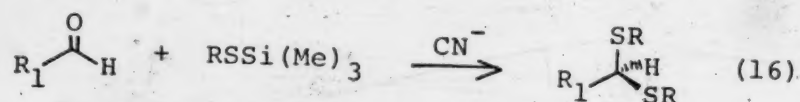


esters^{16b} (eq. (15)), both reactions (14) and (15)

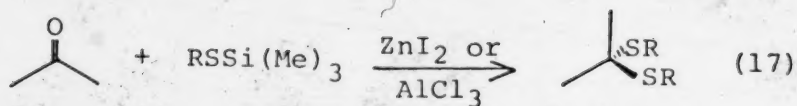


requiring equimolar amounts of aluminum chloride.

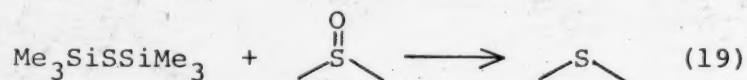
Evans^{17a} has since shown that trimethylsilyl alkylthiolates efficiently convert aldehydes into thioacetals in the presence of trace amounts of cyanide ion (eq. (16)),



and ketones into thioacetals with catalytic amounts of Lewis acid (eq. (17)). Silicon sulfide¹⁰ (eq. (18))

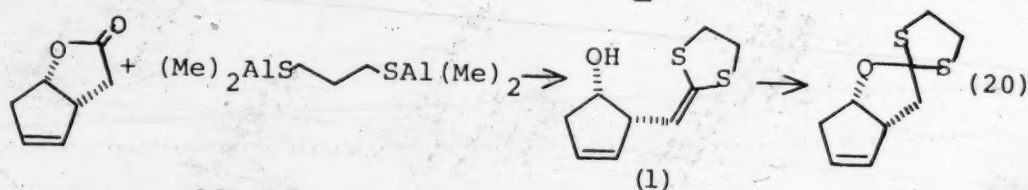


and disilthianes^{17b} (eq. (19)) have been shown to de-

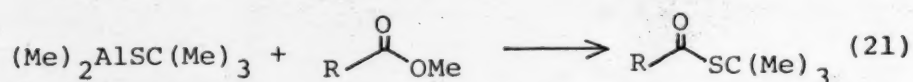


oxygenate sulfoxides.

Aluminum-sulfur compounds have only recently been investigated; the few literature examples indicate that they constitute a powerful set of deoxygenating reagents. Corey showed that bis(dimethylaluminum) 1,2-ethanedithiolate converts lactones into dithiolane ortholactones^{18a} (eq. (20)) by way of a readily isolable ketene thioacetal intermediate^{18b} (1). Lactones^{19a}



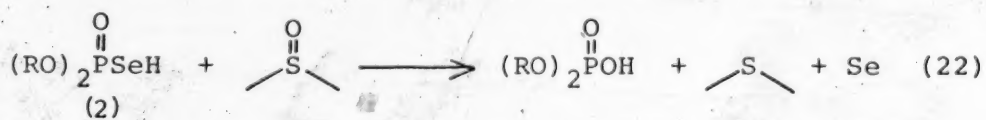
and esters^{18b,19a} are also converted into thioesters by dimethylaluminum alkylthiolate reagents (eq. (21)).



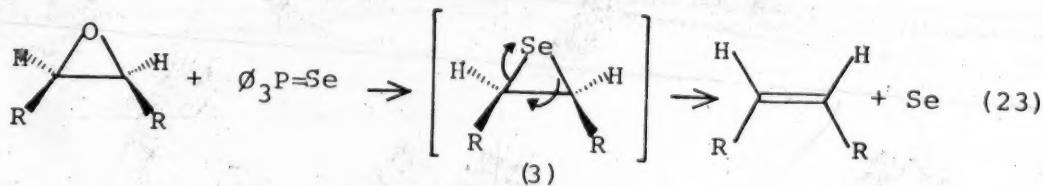
Until the work described in this thesis was undertaken, the use of boron-selenium reagents for organic

transformations had not been reported.

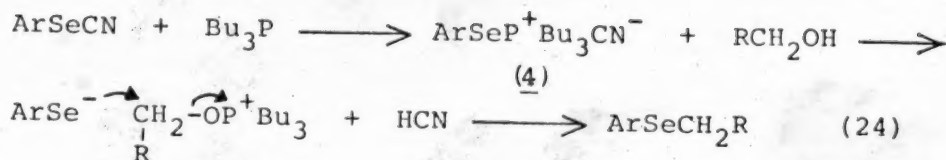
Selenium-phosphorus reagents have received considerable attention. The earliest work to mention the ability of selenium-phosphorous compounds to deoxygenate was by Mikolajczyk²⁰ who showed that O,O-dialkyl hydrogenphosphoroselenoate (2) converted dimethyl sulfoxide into dimethyl sulfide (eq (22)). Contrary



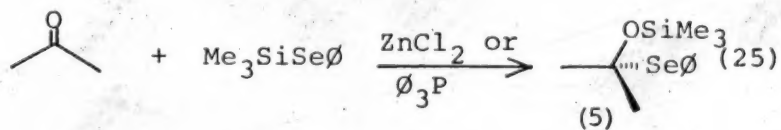
to the analogous sulfur reagent in equation (12), phosphoruspentaselenide (P_4Se_{10}) has been shown to be inert to sulfoxides.¹⁰ Triphenylphosphine selenide undergoes a similar reaction to the analogous sulfur reagent in equation (3), with the added advantage of a spontaneous extrusion process from the episelenide intermediate (3), resulting in a one-step method for converting epoxides into olefins² (eq. (23)). This



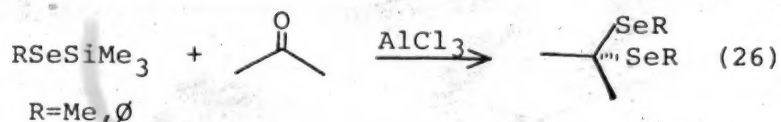
reaction will be discussed in detail later. Finally, Grieco²¹ has developed a method for deoxygenating primary alcohols using a tributylphosphine-selenide complex (4) that is generated in situ from the reaction of selenocyanates with tributylphosphine (eq. (24)).



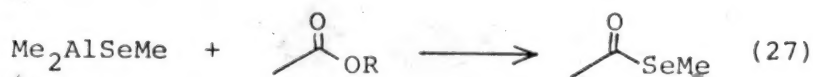
There have been only two reports in the literature on the use of silicon-selenium reagents. It has been observed that trimethylsilyl phenylselenide reacts quantitatively with aldehydes and most ketones by simple addition to give O-(trimethylsilyl)monoselenoacetal (5) in the presence of catalytic amounts of zinc chloride or triphenylphosphine²² (eq. (25)); but



Krief has found that high yields of selenoacetals are available from aldehydes and ketones and selenomethyl or selenophenyl trimethyl silane in the presence of half an equivalent of aluminum chloride²³ (eq. (26)).



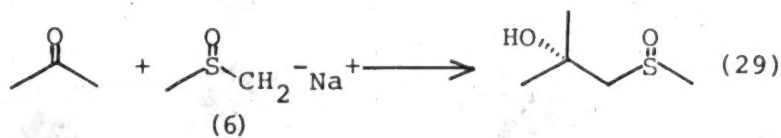
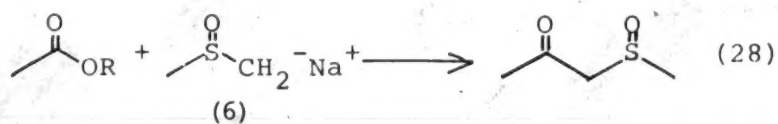
Only one reference to the use of a selenium-aluminum reagent has been made in the literature. Dimethylaluminum methylselenide has been used to convert esters into selenomethyl esters in high yield²⁴ (eq. (27)), in a reaction directly analogous to the



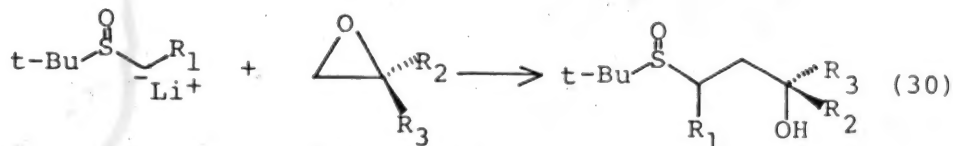
sulfur process of equation (21).

Deoxygenation of Sulfoxides

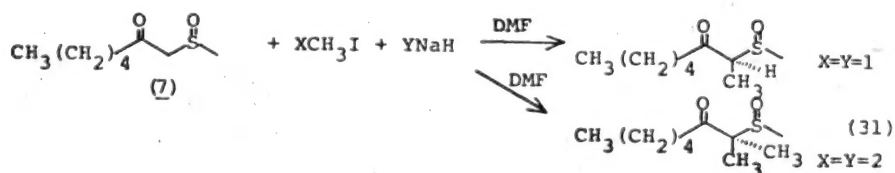
Sulfoxides possess useful properties that make them important intermediates in various synthetic transformations, but the successful application of these procedures generally involves conversion to the sulfide at some stage. One of the most useful properties of sulfoxides is the acidity of the protons alpha to sulfur, and the high nucleophilic character of the alpha-metallated species. The first synthetically important study of these reactions was made by Corey,²⁵ who showed that the methylsulfinyl carbanion (6), generated in dry dimethyl sulfoxide by sodium hydride, was readily acylated by esters (eq. (28)) and alkylated by ketones and aldehydes (eq. (29)). Durst²⁶ observed that the



lithium salts of sulfoxides regiospecifically open epoxides (eq. (30)). Sulfoxide anions have also been

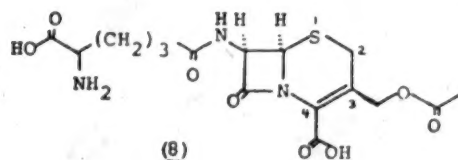


shown to possess high regioselectivity in alkylation; thus, beta-ketosulfoxide (7) was regioselectively mono- or dialkylated with methyl iodide and sodium hydride in dimethyl formamide²⁷ (eq. (31)).

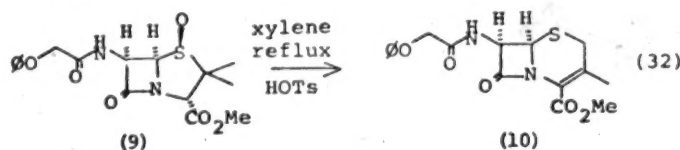


The successful application of the use of sulfoxides as alkyl synthons requires the removal of the sulfoxide moiety in the presence of sensitive functional groups. The most common method involves aqueous tetrahydrofuran solutions over aluminum amalgam.²⁵ Other mild procedures consist of reduction of the sulfoxide to the sulfide, which can then be reduced with Raney nickel, or lithium in amines.²⁸

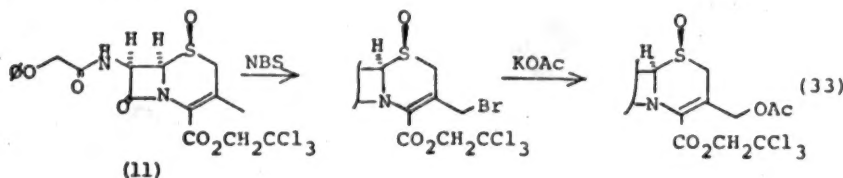
The major effort during recent years has concerned the reduction of sulfoxides in the presence of sensitive functional groups to produce the sulfide itself: specifically in the penicillin and cephalosporin sulfoxide area. Cephalosporin C (8) was discovered in 1953 and attracted immediate interest because of its



effectiveness against organisms which had become resistant to penicillins.²⁹ Morin showed in 1963^{30a} that the sulfoxide of penicillin (9) was converted to the partial cephalosporin structure (10) by treatment with catalytic amounts of toluenesulfonic acid in refluxing xylene (eq. (32)). The conversion was improved to

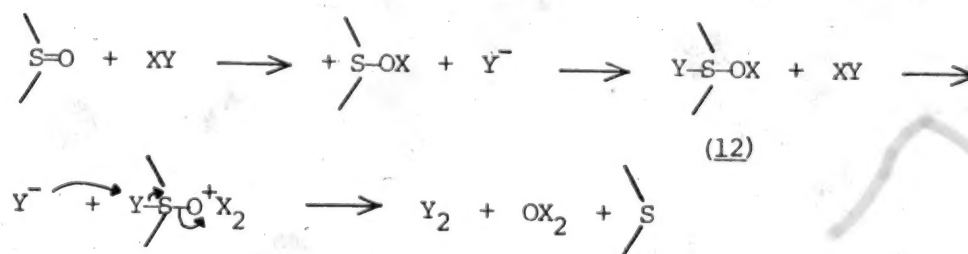


60% yield,^{30b,c} but functionalization of the allylic methyl group to form the naturally occurring acetoxy cephalosporin series could not be done by the usual free radical reactions^{31a} due to preferential attack at the C-2 position. It was found, however, that prior conversion of the cephalosporin into the sulfoxide (11) gave only allylic bromination with *N*-bromosuccinimide and initiator^{31b} and the bromo compound was readily converted into the acetoxy cephalosporin (eq. (33)).



Sulfoxides themselves are apparently readily reduced to sulfides by a wide variety of reagents, and this topic has recently been reviewed³² in a comprehensive manner. The most common type of reaction utilizes a reagent that can bind strongly with oxygen to activate the S-O bond. In most cases, a tetrahedral intermediate (12) has been proposed to form,³³ followed by nucleophilic attack at the thiophile, Y, and cleavage of the S-O and Y-S bonds, as represented in Scheme I. This mechanism has been suggested for

Scheme I



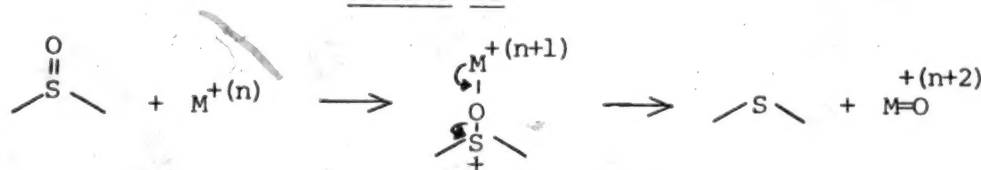
the reduction of sulfoxides by hydrogen iodide (X = H, Y = I), the only system to be studied in detail.³⁴

The most common activating agent used is the proton (in Scheme I, X = H); in this context, sulfoxides have been shown to be reduced by hydrogen chloride,³⁵ hydrogen bromide,³⁶ mercaptans,³⁷ phenylselenol,³⁸ carbothioic acid,³⁹ and mono- and dithiophosphoric acids.⁴⁰ Other agents have been used to activate the S-O bond, and these sulfide

producing reactions probably also proceed by a mechanism similar to Scheme I, although the details have not been studied at this time. These reagents include acetyl chloride (X = Ac in Scheme I) with iodide,⁴¹ acetyl chloride by itself (X = Ac, Y = Cl),⁴² and acetyl bromide;⁴³ trifluoroacetic anhydride (X = CF₃CO-) with iodide;⁴⁴ trimethylsilyl bromide^{45a} and trimethylsilyl iodide⁴⁵ (X = TMS); and oxalyl chloride with iodide.⁴⁶

Low valent metal ions can also reduce sulfoxides, and have been found to be highly chemoselective for the S-O bond³² (Scheme II). The synthetically useful

Scheme II



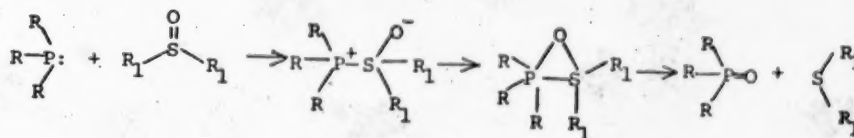
examples include titanium(III),⁴⁷ tin(II),⁴⁸ molybdenum(II),⁴⁹ and vanadium(II),⁴⁹ tungsten(III)⁵⁰ and chromium(II).⁵¹

The reduction of sulfoxides can be accomplished with metallic hydrides, but these reagents usually require activation with a low valent metal. Useful reagents that give high yields of sulfide under mild conditions include dichloroborane⁵² which was found to be highly selective for sulfoxides, sodium borohydride

with cobalt(II) chloride,⁵³ and lithium aluminum hydride with titanium tetrachloride.⁵⁴

The most promising sulfoxide deoxygenating reagents, at least with respect to penicillins and cephalosporins, are those containing phosphorus. Trivalent phosphorus compounds have been shown to be readily oxidized by sulfoxides, with the production of sulfides, liberating phosphine oxides from phosphines,^{55a} phosphates from phosphites,^{55b,c} and phosphorus oxychlorides from phosphorus trichloride.^{55d} The mechanism of the reaction has not been studied thoroughly but that depicted in Scheme III has been proposed^{55c,d} and

Scheme III



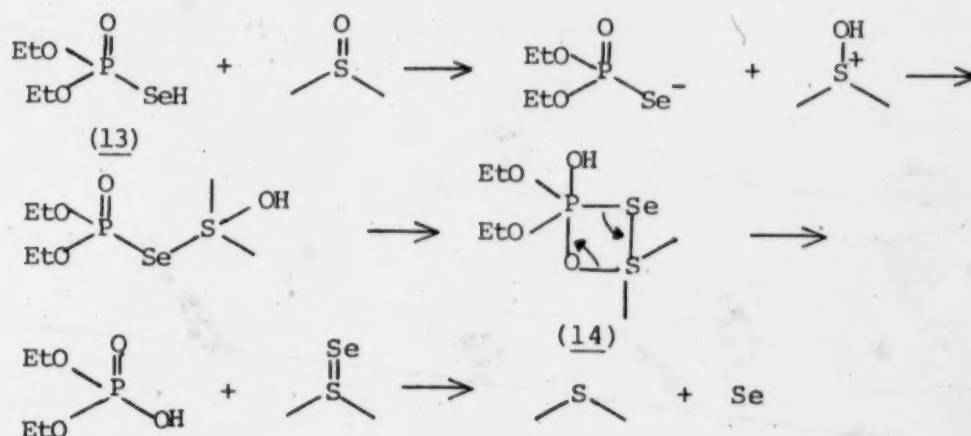
is consistent with the following observations: the rate is inversely proportional to the electron donating ability of R;^{55d} the reaction is catalyzed by acid;^{55a} and no P-Cl cleavage is seen for the trichlorophosphines tested.^{55d} Phosphorus trichloride^{56a} and bromide^{56b,c} convert cephalosporin S-oxides into cephalosporin, although the oxidation products were not identified. Phosphorus pentasulfide has recently been investigated, and has been found to deoxygenate sulf-

oxides giving good yields of sulfides under mild conditions,⁵⁷ and > 90% yields of penicillin and cephalosporin from their respective S-oxides.^{14d} The mechanism of this reaction has received little study.¹⁰

The Phosphorus Selenium Reagent

In 1966²⁰ it was reported that O,O-diethyl hydrogen phosphoroselenoate (13) reacts with an equimolar amount of dimethyl sulfoxide without solvent to give diethyl phosphate, dimethyl sulfide and selenium metal (eq. (22)) in an exothermic reaction at 0°. The proposed mechanism²⁰ involved the formation of an intermediate (14) followed by cleavage of the phosphorus-selenium bond and formation of a sulfur-selenium double bond (Scheme IV). We felt that this reaction deserved

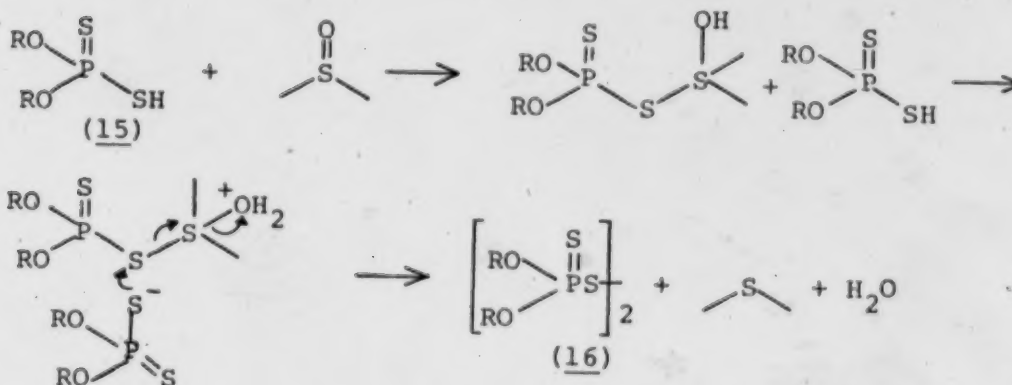
Scheme IV



further investigation, not only as a possible general sulfoxide deoxygenation reagent that gives easily removable byproducts (selenium metal and diethyl phosphate), but due to the unusual course of the reaction.

An analogous sulfur reagent, O,O-dialkyldithiophosphoric acid (15), has been found to efficiently reduce sulfoxides to sulfides, and the reaction has been studied in some detail.^{33c} It is thought to proceed by the mechanism in Scheme V, based mainly on

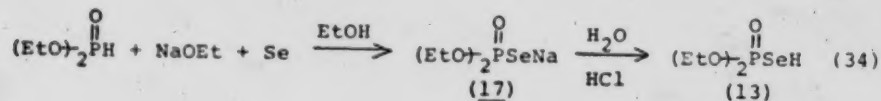
Scheme V



analogy with the hydrogen iodide reaction shown in Scheme I and the quantitative isolation of disulfide (16) from the reaction mixtures. The selenium mechanism of Scheme IV was most unusual in that no diselenide was represented.

Results and Discussion

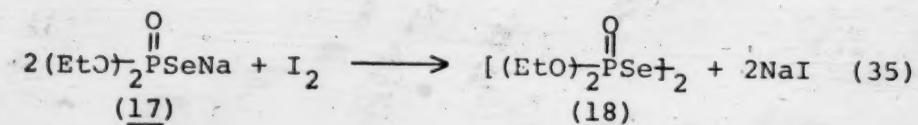
The O,O-diethyl hydrogen phosphoroselenoate (13) was easily prepared according to the method of Markowska and Michalski⁵⁸ from the sodium salt (17)⁵⁹ (eq (34)).



We have found that the acid, a pale yellow oil that is isolated in ca. 90% yield by acidification and extraction into diethyl ether, is quite unstable and turns dark yellow-orange on standing overnight. However, the sodium salt precursor (17) is a white crystalline solid available in 86% yield from diethylphosphite, and our observation is that it can be stored⁶⁰ for as long as one year with no noticeable loss in activity or of yield of the acid (13). The acid (13) itself can be prepared and ready for use in a few minutes, but should be kept under oil pump vacuum for at least an hour to remove traces of solvent if accurately measured quantities are to be dispensed.

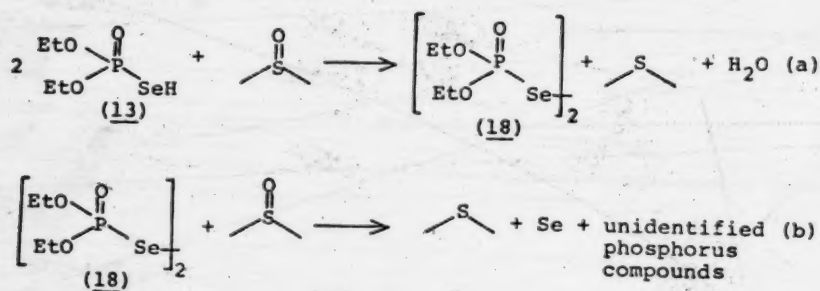
For our initial experiment with the acid (13), we repeated Mikolajczyk's procedure²⁰ using an equivalent amount of dimethyl sulfoxide, except that chloroform was employed as a solvent. Our observations were contrary to Mikolajczyk's, who reported an exothermic reaction and immediate deposition of selenium metal

using neat acid (13) and dimethyl sulfoxide. The chloroform solution immediately turned bright yellow-orange with the evolution of some heat, and then became slightly turbid. The turbidity eventually cleared, forming a small layer on top of the chloroform, which we took to be water. (It was soluble in water and was non-flammable.) The same reaction, done in an NMR tube in deuterated chloroform, showed, after thirty minutes, two signals: a singlet at δ 2.69 due to dimethyl sulfoxide and a singlet at δ 2.09 due to dimethyl sulfide. Integration of the signals indicated the reduction to be 50% complete. On standing overnight, no change in the ratio of dimethyl sulfoxide to dimethyl sulfide was observed by NMR. In another experiment, dimethyl sulfoxide was placed in an NMR tube with 200 mole per cent of acid (13); our observations were the same as above, except that the reduction had gone 93% to completion after thirty minutes and 97% to completion after one hour (based on integration of the dimethyl sulfoxide and dimethyl sulfide signals). Finally, bis(O,O-diethyl phosphoryl)diselenide (18) was prepared by oxidation of the sodium salt (17) with iodine⁵⁹ (eq. (35)). We found that a neat mixture of



the bright yellow-orange diselenide (18) and dimethyl sulfoxide after standing overnight produced a black precipitate, presumably selenium metal, and an NMR measurement of the reaction mixture showed that the dimethyl sulfoxide had been reduced to dimethyl sulfide to a large extent. Our results, summarized in Scheme VI, indicate that the reduction of dimethyl

Scheme VI



sulfoxide with the acid (13) can occur by two distinct processes in the presence of excess (in this case, > 50 mole %) of sulfoxide. The first process (a) is fast and is completely analogous to the dithiophosphoric acid reduction^{33c} of sulfoxides shown in Scheme V. We find the second process (b) to be quite slow, and do not note it to any extent (as judged by the appearance of selenium precipitate) unless the reaction is done with neat reactants. We conclude that Mikolajczyk's procedure of using equimolar amounts of the neat reactants (Scheme IV) resulted in the

release of enough heat from process (a) in Scheme VI to cause the second process (b), reduction of the sulfoxide by the diselenide (18), to occur rapidly.

We next looked at the feasibility of using the acid (13) as a general reducing agent for sulfoxides. Initially, the motivation behind our experiments was that the reduction would proceed as depicted in Scheme IV, with the byproducts of the reaction being readily removed by filtration (selenium metal) and extraction into base (phosphoric acid). Unfortunately, the reduction of sulfoxides by the diselenide (18) proceeded too slowly for this to be a convenient reductive step, so we settled for using two moles of acid (13) per mole of sulfoxide, the problem being removal of the diselenide produced. We found that the diselenide was readily decomposed by base to selenium metal and other unidentified phosphorus products: the diselenide could be removed conveniently by filtration of the reaction mixture through a short alumina column, or by washing methylene chloride solutions with 1 N sodium hydroxide, or diethyl ether solutions with 0.1 N potassium carbonate.

The reduction of a variety of sulfoxides was studied, and the results are summarized in Table II. It can be seen that the reactions are fairly rapid and high yields of sulfide are obtained for the aliphatic

TABLE II. REDUCTION OF SULFOXIDES BY PHOSPHORSELENOATE (13)

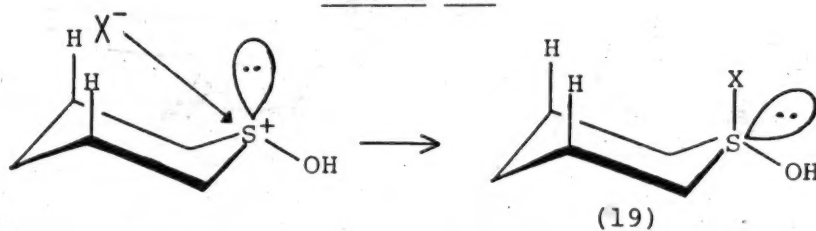
Entry	Sulfoxide	Equivalent of Reagent (13)	Solvent	Temperature	Time (h)	% Yield of Sulfide
1	$\text{Me}_2\text{S=O}$	1	CHCl_3	R.T.	1.0	97 ^a
2	$\text{nBu}_2\text{S=O}$	1.1	CH_2Cl_2	R.T.	1.5	92
3	$(\text{OCH}_2)_2\text{S=O}$	1.61	CH_2Cl_2	R.T.	3	92
4	$\text{O}_2\text{S=O}$	2.17	CH_2Cl_2	reflux	28	94
5	$(p\text{-MeC}_6\text{H}_4)_2\text{S=O}$	1.3	CHCl_3	35°C	1.5	78
6	$-(\text{CH}_2)_5\text{S=O}$	1.62	CHCl_3	R.T.	2.25	74
7	$(t\text{Bu})\text{MeS=O}$	2.9	CH_2Cl_2	reflux	25	79 ^b
8	$t\text{Bu}_2\text{S=O}$	2.11	CHCl_3	reflux	14	14 ^b

a. Yield determined by NMR.

b. Yield determined by VPC against an internal standard.

sulfoxides (entries 1, 2, 3, Table II). Two drawbacks of the reagent (13) are: its sensitivity to electronic effects, as seen by the lower yield for *p*-tolyl methyl sulfoxide (entry 5) and the prolonged reaction time needed for diphenyl sulfoxide (entry 4); and its sensitivity to steric effects, as seen by the prolonged reaction time needed for methyl *t*-butyl sulfoxide (entry 7) and low yield of di-*t*-butyl sulfoxide (entry 8). The modest yield for pentamethylene sulfoxide (entry 6) can be explained in terms of a steric effect. A decrease in rate was observed^{34b} for the acid catalyzed reduction of pentamethylene sulfoxide by iodide ion, and it was proposed^{34b} that the angle of approach needed to form a tetracoordinate intermediate (19) by iodide ion ($X = I$) is severely restricted by interaction of the axial hydrogens (Scheme VII). By

Scheme VII



the same reasoning, the reaction of (13) with pentamethylene sulfoxide ($X = >P(=O)-Se$) is expected to be hindered.

Several promising reagents have recently appeared

for the reduction of sulfoxides, and are summarized in Table III. Of these, the drawbacks of phosphorus-pentasulfide, trimethylsilyl iodide, and phenyltrimethylsilane are obvious. Dichloroborane has been shown to be quite selective for sulfoxides in the presence of ketone and esters, but a prolonged reaction time is required for reduction of diphenyl sulfoxide. The lithium aluminum hydride—titanium tetrachloride system gives excellent yields for the sulfoxides noted, but its selectivity for sulfoxides has not been demonstrated; the trimethylsilyl chloride-sodium iodide system also gives high yields, but steric requirements and selectivity in the presence of ethers and esters remain to be demonstrated. The trifluoroacetic anhydride—sodium iodide system is clearly a good reducing agent, and the reaction has been reported to be instantaneous at 0° for all examples tested; its selectivity still needs to be shown.

The hydrogen phosphoroselenoate (13) did not fulfill our expectations for the deoxygenation of sulfoxides; however, our observation of the nucleophilicity of the sodium salt (17) eventually led to the development of a remarkable phosphorus-tellurium deoxygenation reagent that will be dealt with later. At present, we will continue the discussion of sulfoxide deoxygenation with a description of another

TABLE III. SOME OTHER REAGENTS FOR REDUCING SULFOXIDES

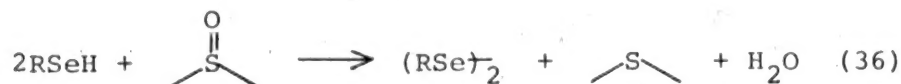
Sulfoxide	Reagent	(CF ₃) ₂ C=O, NaI ⁴⁴	P ₄ S ₁₀ ⁵⁷	Me ₃ SiH ^{45a}	Me ₃ SiO, I ₂ ^{45a}	Cl ₂ BH ⁵²	LiAlH ₄ , TiCl ₄ ⁵⁴	(EtO) ₂ P-SH ⁶¹	(EtO) ₂ PSeH ⁶¹	Me ₃ SiCl, NaI ^{45b}
(CH ₃) ₂ S=O	Time Temp Yield	< 1 min 0° 93%	4 hr R.T. 61%	decomposes	6 hr 130° 81%	---	2 hr R.T. 89%	3 hr R.T. 92%	40 min -15° 91%	
φ ₂ S=O	Time Temp Yield	< 1 min 0° 99%	16 hr R.T. 73%	2 hr R.T. 73%	8 hr 130° 83%	24 hr 25° 90%	2 hr R.T. 83%	12 hr R.T. Quant. ^a	20 min R.T. 95%	
(p-MeC ₆ H ₄) (t-Bu)S=O	Time Temp Yield	< 1 min 0° 96%	---	---	---	---	4 hr R.T. 90%	---	---	
(t-Bu) ₂ S=O	Time Temp Yield	---	---	---	---	---	---	14 hr 65° 14%	---	

a. Reaction done without solvent.

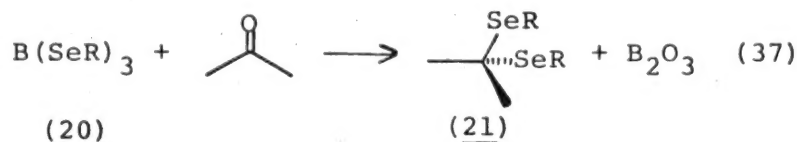
selenium compound containing an atom known for the strength of its bonds to oxygen.

The Boron-Selenium Reagents

Selenols have been shown to reduce sulfoxides to sulfides³⁸ in a process (eq. (36)) similar to the



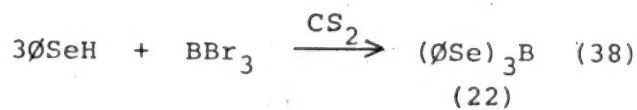
one shown in Scheme V. We had already found that tris-(alkylseleno)boranes (20) were superior to selenol-acid mixtures²³ for the preparation of alkylseleno-acetals (21) from ketones, aldehydes and acetals (eq. (37)), and it seemed reasonable that these reagents⁶²



might work well for sulfoxides.

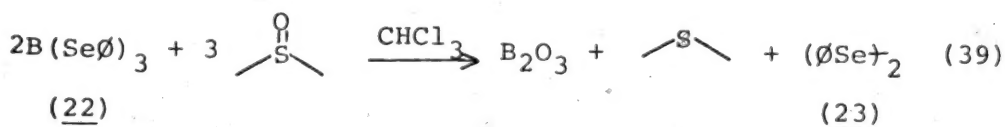
Results and Discussion

We used tris(phenylseleno)borane (22) for all our initial work on the sulfoxide reductions. The borane (22) is readily available in 74% yield as a pale yellow crystalline solid from the reaction of benzeneselenol with boron tribromide^{62a} (eq. (38)). The reagent (22) is easily stored for long periods of time, as long



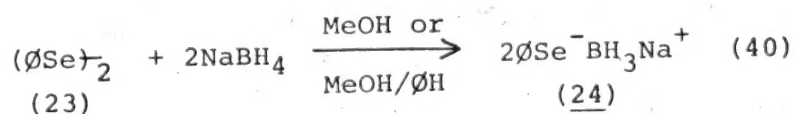
as adequate precautions are taken to protect it from atmospheric moisture.⁶³ We have found it convenient to make transfers of the reagent (22) inside a plastic glove bag flushed with dry nitrogen in order to prolong activity. The borane (22) is very soluble in chloroform and methylene chloride, and these solvents were suitable for all our reactions.

The phenylseleno-reagent (22) reacts vigorously with most sulfoxides; addition of sulfoxide to the borane solution produces a dark yellow color accompanied by a gelatinous precipitate and the evolution of heat. The yellow color was identified as being due to diphenyldiselenide (23) (by thin layer chromatography) and the precipitate was presumed to be an oxide of boron. From this we concluded that the reaction proceeds according to equation (39).



Upon completion of the reduction, the precipitate was easily removed by filtration or washing with water. In our early experiments, the diphenyl diselenide (23)

was removed by chromatography. Later, however, we found that the diselenide (23) could be removed more conveniently by conversion to its anion (24). Thus, treatment of a methanol or benzene/methanol solution of the reaction mixture with sodium borohydride until a colorless solution was obtained⁶⁴ (eq. (40)), and

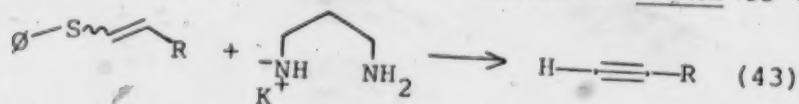


then immediate partitioning between pentane/water or ether/water nearly quantitatively removed the water soluble anion (24).

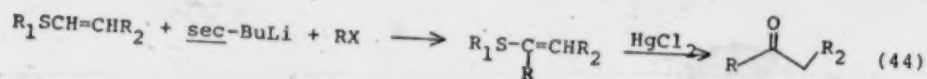
The sulfoxide reduction (eq. (39)) with phenylselenoborane (22) was tried on a variety of simple mono- and difunctional sulfoxides in order to test the power and selectivity of the reagent (22); the results are summarized in Table IV.

We concluded that the reagent (22) is a powerful sulfoxide reducing agent, as is indicated by the excellent yield of dibenzyl sulfide obtained under very gentle conditions (entry 1a). More vigorous conditions were needed for the reduction of diphenyl sulfoxide (entry 2) and di-*t*-butyl sulfoxide (entry 3), but the yields of sulfides, as judged by vapor-phase chromatography with an inert internal standard, were excellent and good, respectively, with short reaction

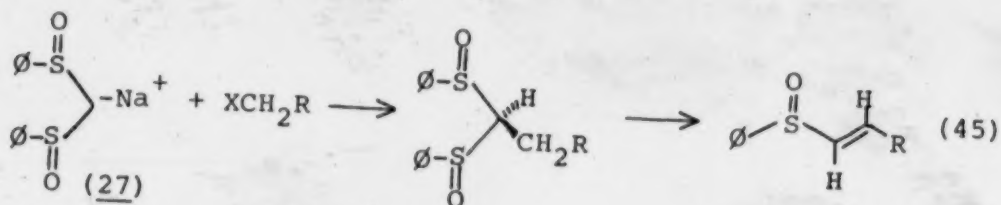
which can be converted into terminal acetylenes by treatment with strong bases⁶⁶ (eq. (43)); and have been shown to be deprotonated and alkylated alpha to the



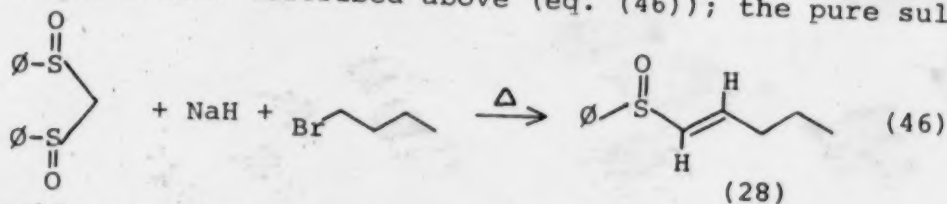
sulfur atom. The latter process affords ketones⁶⁷ (eq. (44)). Vinyl sulfoxides are reported to be avail-



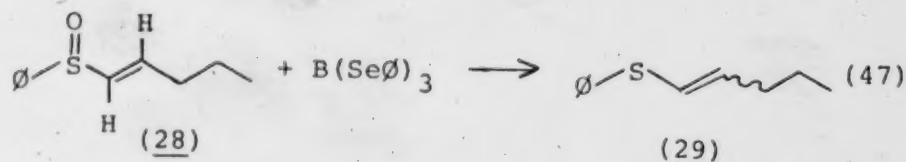
able in fair yield by alkylation of the bis(phenylsulfinyl)methyl anion (27) and pyrolysis of the resulting bis sulfoxide⁵ (eq. (45)).



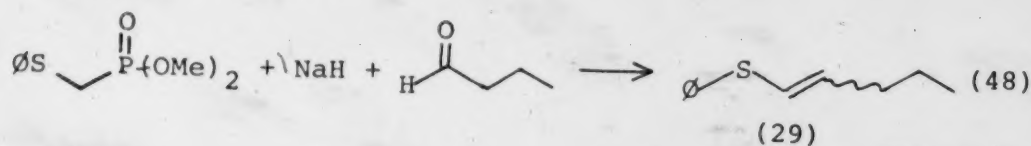
(E)-1-(Phenylsulfinyl)-1-butene (28) was prepared in the manner described above (eq. (46)); the pure sulf-



oxide was identified as the trans isomer by the coupling constant of the vinyl protons ($J = 15 \text{ Hz}$).⁶⁸ The reduction of sulfoxide (28) with borane (22) went smoothly at 0° (eq. (47)), and a high yield of the sulfide (29) was isolated (entry 4). However, although

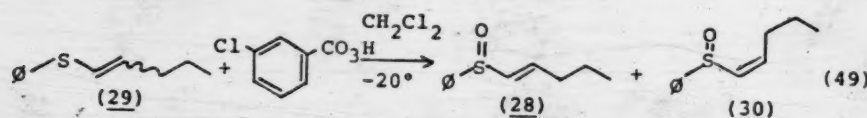


NMR spectrum of (29) was consistent with the proposed structure, the signals in the olefinic region (δ 5.7 - 6.2) were far too complex to represent only trans isomer.⁶⁸ Vinyl sulfide, prepared by an alternate route using a Horner-Wittig reaction⁶⁹ (eq. (48)) was



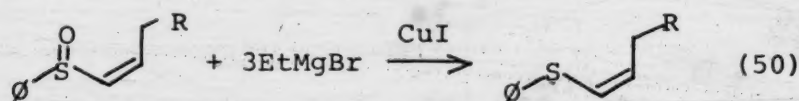
physically and spectrally identical to the sulfide product from equation (47); the vinyl regions of the NMR spectra of the products from equations (47) and (48) were almost superimposable, implying similar isomeric composition from the two reactions. We could not analyze the product of equation (47) because the starting sulfoxide (28) was very difficult to make and isolate, contrary to the literature claims.⁵ Since the sulfide (29) from equation (48) was available in larger quantities than the product from the borane reduction (eq. (47)), the composition of (29) from equation (47) was deduced from an analysis of the composition of the product from the Horner-Wittig reaction (eq. (48)).

Sulfide (29) (from equation (48)) was oxidized by meta-chloroperbenzoic acid to a mixture of E (28) and Z (30) vinylsulfoxides (eq. (49)) that were easily



separated by chromatography on alumina. The sulfoxides, which were obtained in almost equal amounts (75% overall yield), were identified on the basis of the vinyl coupling constants from the proton NMR: for (28), $J_{\text{vinyl}} = 15$ Hz; for (30), $J_{\text{vinyl}} = 9.5$ Hz. We conclude that the reduction of vinyl sulfoxides with phenylselenoborane (22) is not stereoselective.⁷⁰

Since the publication of this work, a report appeared on the stereospecific reduction of vinyl sulfoxides with ethyl magnesium bromide/cuprous iodide⁶⁸ (eq. (50)). Although high yields of sulfides were



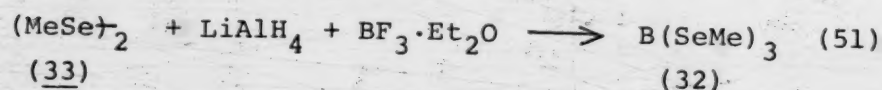
reported, the reagent has yet to be tested on sulfoxides containing Grignard-sensitive functionalities.

It was reported, during our studies, that selenomethyl dimethylaluminum (eq. (27)) converts esters into methylseleno-esters, and so we were curious to see if the phenylseleno reagent (22) would undergo the

same reaction. A chloroform solution of (22) was inert to methyl palmitate (entry 6b) while still possessing the capacity to reduce dibenzyl sulfoxide (entry 6a) in high yield, 12 hours after addition of the ester. Ironically, we found that selenomethyl dimethylaluminum did not reduce dibenzyl sulfoxide.

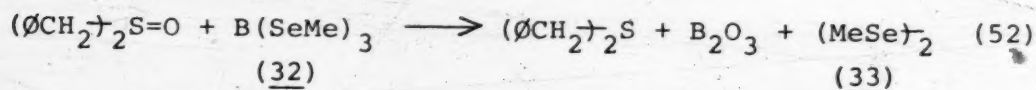
Finally, the deoxygenation of cephalosporin β -sulfoxide methyl ester (31) (See entry 7, Table IV) was attempted using the phenylselenoborane reagent (22). To our surprise, the reagent (22) was completely inert to (31) under the conditions used to deoxygenate di-*t*-butyl sulfoxide (entry 3); more drastic conditions (prolonged refluxing chloroform) caused decomposition of sulfoxide (31), as judged by thin layer chromatography.

From our selenoacetal work we had found that tris(methylseleno)borane (32) was superior in many cases to the phenylselenoborane reagent (22) for the deoxygenation of aldehydes and ketones. The reagent (32) is readily prepared in 70% yield from dimethyl diselenide (33), lithium aluminum hydride, and boron trifluoride etherate (eq. (51)). The reduction of



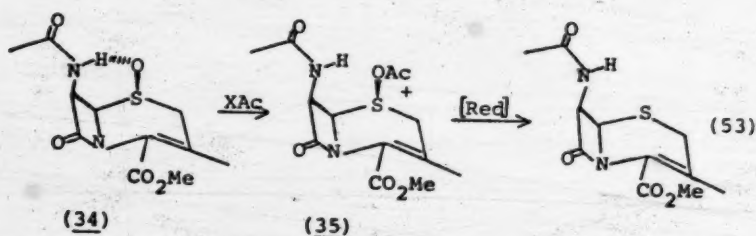
dibenzyl sulfoxide (entry 1b) by (32) required more vigorous conditions than were needed for the phenyl-

seleno-reagent (22) (entry 1a); but the reaction (eq. (52)) went smoothly, and (32) has the added advantage



that the diselenide (33) is volatile, and may be removed easily from nonvolatile sulfides by evacuation. This reagent (32) also failed to react with cephalosporin sulfoxide (31). Under vigorous conditions only decomposition of the cephalosporin was observed.

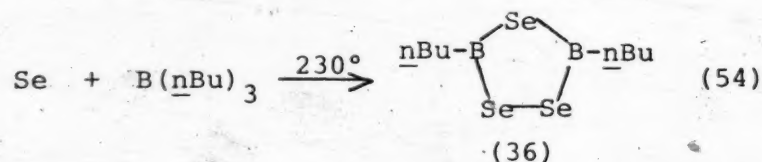
For the penicillin beta-sulfoxide series, it has been shown that there is a strong interaction between the amide proton and the sulfoxide oxygen;⁷¹ a similar interaction is probable for cephalosporin beta-sulfoxides as shown for (34) in equation (53). Kaiser^{56a} has



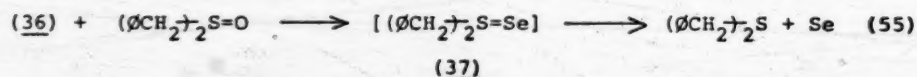
found that cephalosporin beta-sulfoxides are readily reduced only in the presence of "activating" agents, such as acid halides (eq. (53)), and suggests that this is due to an initial reaction of the sulfoxide oxygen, as represented by (35). Thus, a suitable reducing agent for cephalosporin beta-sulfoxides must initially break

the hydrogen-oxygen interaction shown in (34). It is possible that the Lewis acidities of the reagents (22) and (32) are too low for this purpose.

In order to continue the cephalosporin sulfoxide deoxygenation study, another boron-selenium reagent was investigated. 3,5-Di-*n*-butyl-1,2,4,3,5-triselenodiborolane (36) was readily obtained in 89% yield as a bright yellow liquid from selenium metal and tri-*n*-butylborane⁷² (eq. (54)). The observation that the



deoxygenation of dibenzyl sulfoxide with (36) was almost instantaneous at -60° , as judged by NMR, implied that (36) was easily the most powerful sulfoxide deoxygenation reagent that we had tested. However, the reduction (eq. (55)), is not nearly as clean as with the other

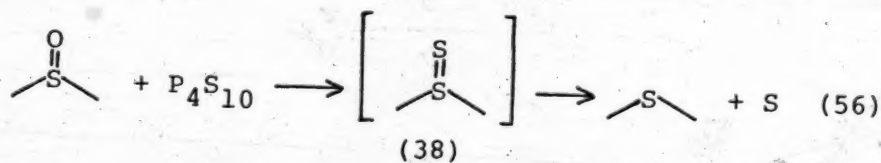


two boron reagents (22) and (32). This can be seen from the lower yield of dibenzyl sulfide (entry 1c). No attempt was made to isolate any byproducts.

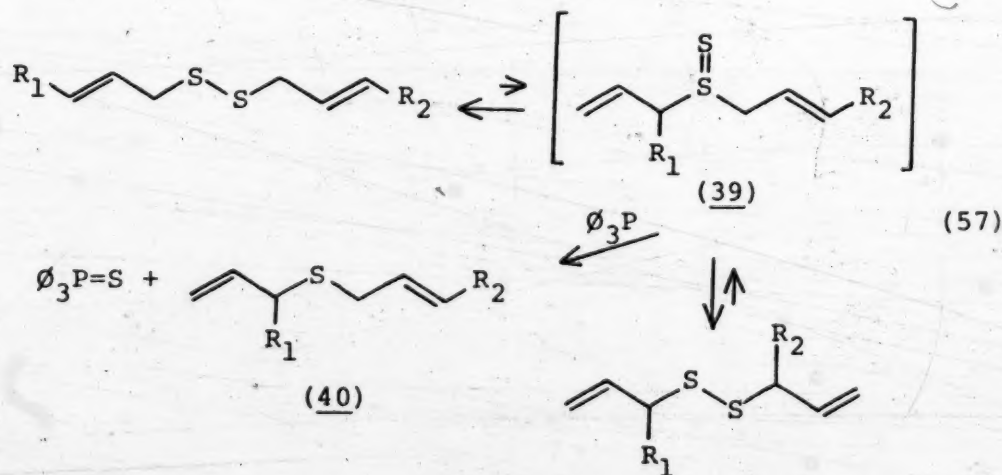
Early in the investigation of the reducing ability of (36), the observation was made that red selenium immediately precipitated from the solution when dibenzyl

sulfoxide and (36) were combined. If, however, the reaction (eq (55)) was done at low temperatures ($< -30^{\circ}$), a bright yellow solution resulted; on warming ($> -30^{\circ}$), red selenium precipitated as before. It occurred to us that the reaction (eq. (55)) could be going through an unstable selenosulfoxide intermediate (37) that decomposes to sulfide and selenium metal on warming.

Intermediates analogous to (37) have been postulated for the deoxygenation of sulfoxides with phosphoruspentasulfide, boron trisulfide, and silicon sulfide¹⁰ (eq. (56)); but the intermediate (38) has



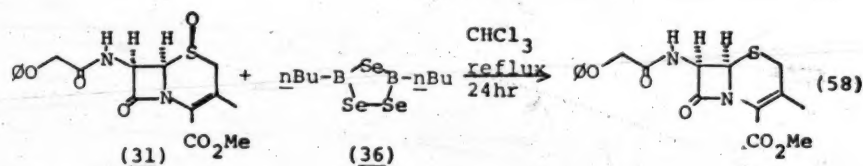
never been detected, the only evidence coming from the observation of facile interconversion of allylic disulfides⁷³ (eq. (57)), and the ability to isolate



allylic sulfides (40) from the allylic disulfides by reaction of the postulated intermediate (39) with triphenyl phosphine, a reaction unknown for dialkyl disulfides.^{73a}

Our own attempts to identify the intermediate (37) were also unsuccessful, as an NMR spectrum (100 MHz) of the reaction (eq. (55)) run at -60° clearly showed a singlet at δ 3.5 due to dibenzyl sulfide as the only signal from benzylic protons. We concluded that the two observed stages of the reduction (eq. (55)) were due to reactions of the reagent (36) occurring after sulfide formation.

The boron reagent (36) did successfully deoxygenate cephalosporin beta-sulfoxide (eq. (58)); however the results were not nearly as good as we would like (entry

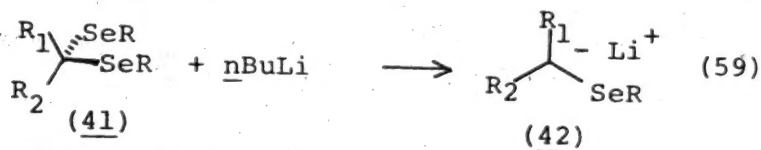


7) and it is clear that the vigorous conditions needed for the reduction (100% excess of reagent (36), chloroform reflux) and the prolonged reaction time (24 h) resulted in extensive decomposition of the product and/or the starting sulfoxide.

Preparation of Selenoacetals

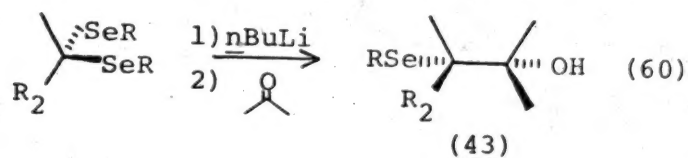
Selenoacetals, represented by (41) in equation (59)), have been known since 1926;⁷⁴ but these compounds have only recently been found to possess properties that make them valuable intermediates for organic transformations.

The efficient production of the selenium stabilized anion (42) from the reaction of *n*-butyllithium with selenoacetals (41) (eq. (59)) has been known since

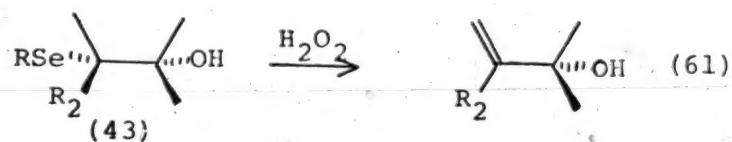


R = ϕ , alkyl
R₂ = H, alkyl

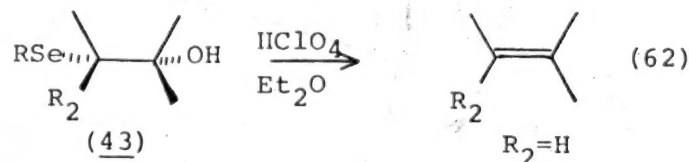
1972,⁷⁵ and the highly nucleophilic character of the anion (42) was shown at that time. Using the anion (42), the methodology has since been developed for the preparation of beta-hydroxylselenides (43)⁷⁶ (eq. (60)), which are synthetically equivalent to:



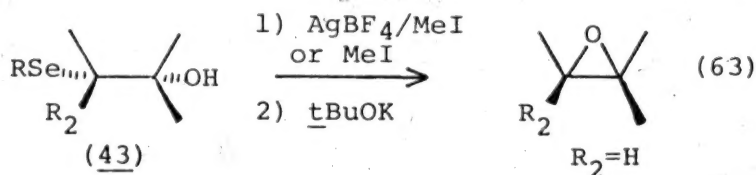
allylic alcohols by oxidation^{77a,b,c} (eq. (61)); olefins



by treatment with strong acids^{77d} (eq. (62)); and



epoxides^{77e} by treatment with methyl iodide and silver tetrafluoroborate^{77f} ($\text{R} = \emptyset$) or methyl iodide alone,^{77g} ($\text{R} = \text{Me}$) followed by the addition of strong base (eq. (63)). The anion (42) has also been employed

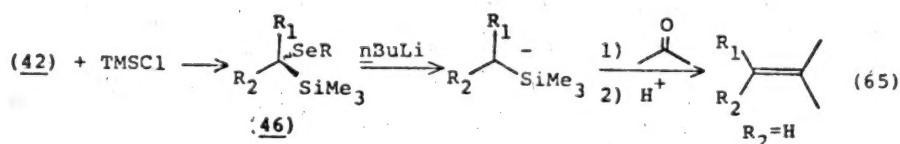


for the convenient preparation of other heteroatom-stabilized carbanions for use in further transformations.

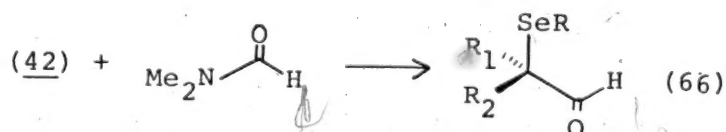
Thus, the anion (42) forms a seleno-thioacetal (44) from the reaction with disulfides which, by treatment with another equivalent of *n*-butyl lithium, gives the sulfur stabilized anion (45) that can be converted into substituted sulfides by treatment with electrophiles^{77b,78} (eq. (64)). In the same manner, silicone stabilized



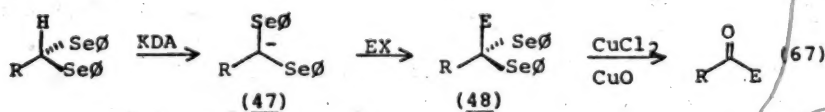
carbanions (46) can be prepared, and these are synthetically equivalent to olefins from reaction with ketones and aldehydes^{77g,79} (eq. (65)). The anion (42) has also been found to attack a variety of acyl



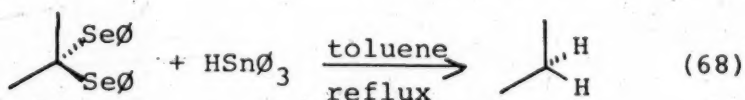
equivalents⁸⁰ (eq. (66)).



Selenoacetals of aldehydes have been deprotonated by strong hindered bases to give the selenium stabilized anion (47):⁸⁰ electrophilic attack on (47) gives a substituted selenoacetal (48),⁸⁰ which is available for any of the transformations listed above, or can be hydrolyzed to a ketone⁸¹ (eq. (67)).

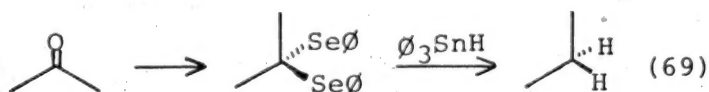


Our interest in selenoacetals was initiated by the discovery in our laboratory that selenoacetals are reduced by triphenyl tin hydride giving high yields of hydrocarbon⁸² (eq. (68)). We have since noted that

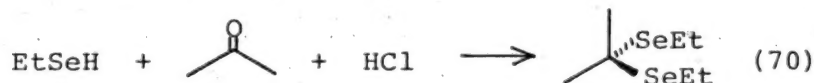


the reduction in equation (68) occurs in the presence of thioacetals and ketones without the loss of these

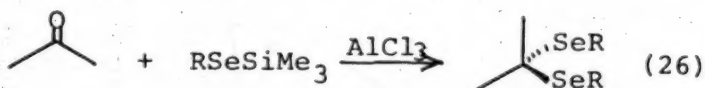
functionalities;⁸³ therefore, with an efficient method for the preparation of selenoacetals from carbonyls, a mild and selective two step procedure for the reduction of carbonyls to hydrocarbons would be available (eq. (69)).



Several reports have appeared on the preparation of selenoacetals from carbonyls, with no obvious advantages over the original preparation from ketone, selenol, and hydrogen chloride⁷⁴ (eq. (70)). The recent



methods include: use of ketone or aldehyde and selenol without solvent with continuous passage of dry hydrogen chloride through the reaction mixture^{75,77g} as in equation (70); the use of ketone or aldehyde, selenol, and sulfuric acid (one mole per mole carbonyl compound) or zinc chloride (half mole per mole carbonyl compound) without solvent;⁶² and the use of carbonyl compound trimethylsilyl alkylselenide, and aluminum chloride²³ (eq. (26)). No details or examples were given for

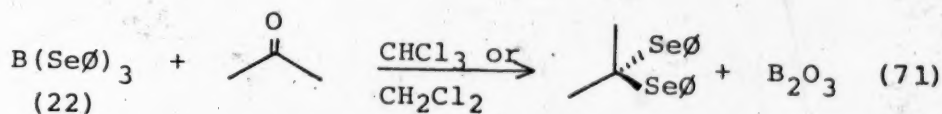


equation (26). High yields of selenoacetals were isolated for most of the ketones and aldehydes reported

in the references cited above, but it should be pointed out that none of the reactions were performed on molecules containing functional groups other than carbonyl. Therefore we decided to investigate two promising selenol equivalents: tris(phenylseleno)borane (22) and tris(methylseleno)borane (32).

Results and Discussion

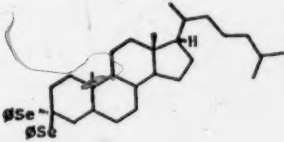
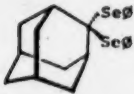
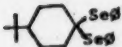
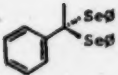
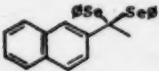
Our initial investigations were with tris(phenylseleno)borane (22), since its physical characteristics (crystalline solid) described in the previous chapter make it convenient to prepare and use. The reagent (22) reacted with ketones according to equation (71),



forming selenoacetals and a similar gelatinous precipitate to that observed in sulfoxide deoxygenations, presumably boron oxides. The results with the phenylselenoborane (22) are summarized in Table V.

The first two ketones that were tried, cholestan-3-one (entry 1) and adamantan-2-one (entry 2), reacted smoothly with (22) and high yields of the selenoacetals were isolated, although the reaction was somewhat sluggish for adamantanone. However, the reaction of (22) with other simple carbonyl compounds gave only

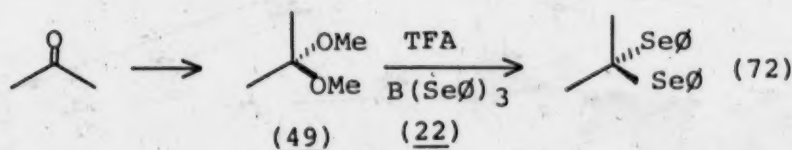
TABLE V.
PREPARATION OF BIS (PHENYLSELENO) ACETALS
FROM CARBONYLS AND (22)

<u>Entry</u>	<u>Product</u>	<u>Time</u>	<u>Mole % TFA</u>	<u>Yield</u>
1		2.5 hr 40 min	0 10.2	89% 88%
2		24 hr 1 hr	0 8.6	84% 63%
3	$(C_4H_9)_2C \begin{matrix} \nearrow \text{Se}\phi \\ \searrow \text{Se}\phi \end{matrix}$	1 hr	10.6	73%
4	$C_{10}H_{21}CH \begin{matrix} \nearrow \text{Se}\phi \\ \searrow \text{Se}\phi \end{matrix}$	1 hr	7	79%
5		18 hr	3.4	80%
6		3 hr	3.8	48%
7		1 hr	9	52%
8		3.5 hr	2.2	28%

complex reaction mixtures, as judged by thin layer chromatography.

It was found that improved yields of selenoacetals could be isolated in most cases by the addition of small amounts of acid to the reaction mixture. While at least one other acid⁸⁴ was observed to be suitable, we found it convenient to use trifluoroacetic acid (TFA) in all of our experiments as it is easily dispensed via syringe into a septum-covered flask. The acid definitely acts as a catalyst for these reactions, as seen by the shortened reaction time needed for cholestanone in the presence of TFA (entry 1). In at least one case, the acid had a detrimental effect: for adamantanone (entry 2), a large amount of unidentified byproduct was observed in the presence of TFA. Even in the presence of TFA, the phenylselenoborane reagent (22) was not suitable for the conversion of aromatic ketones (entries 7 and 8) or cyclopentanone (entry 6) into selenoacetals in high yields.

Improved yields of selenoacetals were observed in all cases if the carbonyl compound was first converted into an oxygen acetal (49) and then the reaction (eq. (72)) performed as an acetal exchange of (49) with



the boron reagent (22). The results of the acetal exchange reactions are summarized in Table VI. The yield enhancement is especially conspicuous for the aromatic selenoacetals (entries 3 and 4); it can be seen that in these cases the yields by the exchange route are good while those involving direct reaction of the carbonyl compound are poor.

The exchange reaction is not suitable for the preparation of phenylselenoorthoesters (entries 6 and 7). The preparation of tris(phenylseleno)methane (entry 6) went smoothly but required an inordinately long reaction time. The preparation of 1,1,1-tris(phenylseleno)ethane (entry 7) occurred in poor yield even in the presence of large amounts of TFA. Attempts to follow the reaction of entry 7 by NMR in the presence of varying amounts of acid resulted in the observation of a larger number of signals than could be accounted for from a simple stepwise exchange process (eq. (73)),

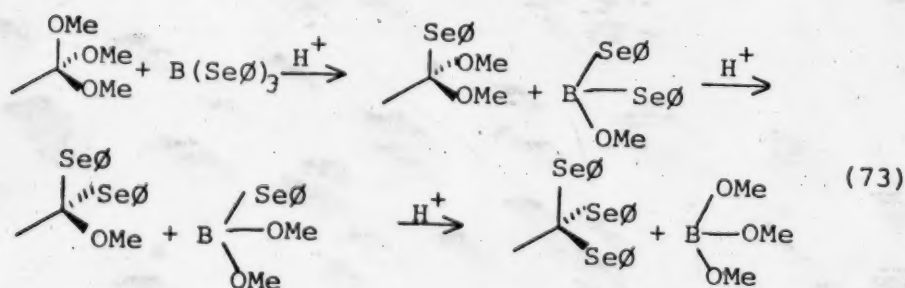
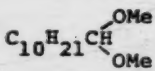
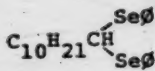
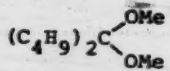
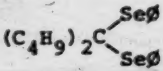
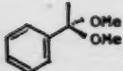
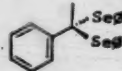
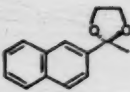
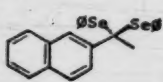
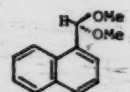
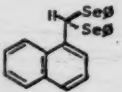


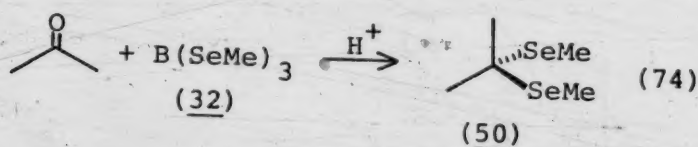
TABLE VI
ACETAL EXCHANGE REACTION WITH (22)

<u>Entry</u>	<u>Acetal</u>	<u>Product</u>	<u>Time</u>	<u>Mole % TFA</u>	<u>% Yield</u>
1			1.5 hr	19	85
2			1.5 hr	17	83
3			3 hr	10	80
4			2 hr	1	71
5			3 hr	4	89
6	HC(OMe)_3	HC(Seo)_3	12 hr	2.7	76
7	$\text{CH}_3\text{C(OMe)}_3$	$\text{CH}_3\text{(Seo)}_3$	5.5 hr	144	25

implying the competition of a number of side reactions.

For the acetals of an aliphatic aldehyde (entry 1) and ketone (entry 2), the efficiency of the exchange reaction (eq. (72)) was found to be quite sensitive to the amount of acid that was added; in fact, substantially more acid was required for the preparation of these two selenoacetals (entries 1 and 2) by the exchange reaction than was needed for direct formation of the selenoacetals from the parent carbonyl compounds (eq. (71)), (entries 3 and 4, Table V). The effect of the acid in these reactions will be described in greater detail later.

Although the sequence represented in equation (72) proved to be highly efficient for the preparation of phenylselenoacetals, methylselenoacetals (50) can be prepared directly from the parent carbonyls (eq. (74)) in yields comparable to those of the exchange



reaction (eq. (72)).

Tris(methylseleno)borane (32) is a liquid that can be conveniently stored in, and dispensed from, a greased syringe. We found that (32) could be stored in this manner for as long as a month with no apparent loss in activity.

The results using the methylseleno-reagent (32) for the preparation of methylselenoacetals (50) from carbonyls (eq. (74)) are summarized in Table VII. All of the ketones tested with (32) were rapidly converted into selenoacetals, in the presence of small amounts of acid. Excellent yields of selenoacetals were isolated, especially for 2-acetylnaphthalene (entry 5) and cyclopentanone (entry 4). The yields were lowered somewhat, and prolonged reaction times were required for the hindered ketones pregnenolone acetate (entry 7) and estrone methyl ether (entry 8), but the products were isolated without cleavage of the acetate ester or methyl ether functionalities. The reaction of cholest-4-ene-3-one (entry 9) with (32) gave a low yield of an unstable white crystalline solid that decomposed at an appreciable rate even on storage at -10° under nitrogen. The product was identified tentatively as the selenoacetal shown (entry 9) by NMR and exact mass measurement, and by conversion into cholest-4-ene by tin hydride reduction (eq. (75)).

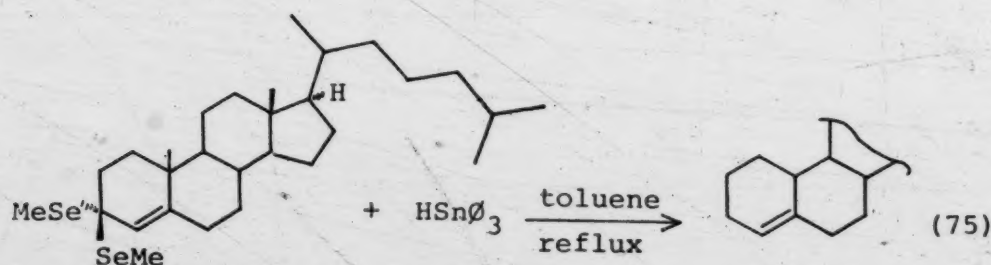
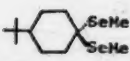
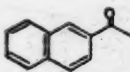
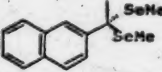
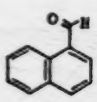
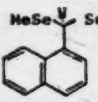
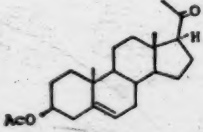
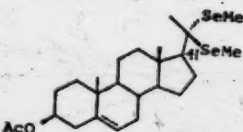
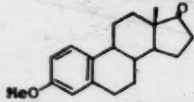
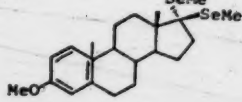
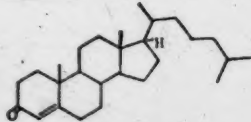
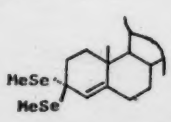


TABLE VII. PREPARATION OF BIS(METHYLSELENO)ACETALS

FROM CARBONYLS AND (32).

Entry	Carbonyl	Product	TFA (mole %)	Time	% Yield
1	$(C_4H_9)_2C=O$	$(C_4H_9)_2C \begin{smallmatrix} \text{SeMe} \\ \text{SeMe} \end{smallmatrix}$	7.8	45 min	90
2	$C_{10}H_{21}CHO$	$C_{10}H_{21}CH \begin{smallmatrix} \text{SeMe} \\ \text{SeMe} \end{smallmatrix}$	66	31 hr	66
3			4.3	50 min	90
4			4.0	20 min	96
5			4.1	2 hr	85
6			4.6	35 min	92
7			19	26 hr	79
8			5.6	3.5 hr	58
9			26	19 hr	31
10	$CH_3C(OMe)_3$	$CH_3C(SeMe)_3$	7.5	13 hr	39%

The reagent (32) was found to be inferior to the phenylselenoborane (22) for the preparation of selenoacetals from aliphatic aldehydes (entry 2), as judged by the respective reactions with undecaldehyde (compare entry 4, Table IV); we found that a modest yield of the methylselenoacetal of the aldehyde (entry 2) could be isolated only after the addition of a large amount of TFA and a prolonged reaction time. On the other hand, the aromatic aldehyde 1-naphthaldehyde was rapidly converted into its methylselenoacetal in excellent yield by (32) (entry 6).

Finally, only a low yield of methylselenoorthoester (entry 10) was isolated from the orthoester exchange reaction (eq. (73)) of (32) with 1,1,1-tris(methoxy)ethane; thus, neither boron reagent (22) or (32) appears to be efficient for this exchange reaction (compare entry 7, Table V).

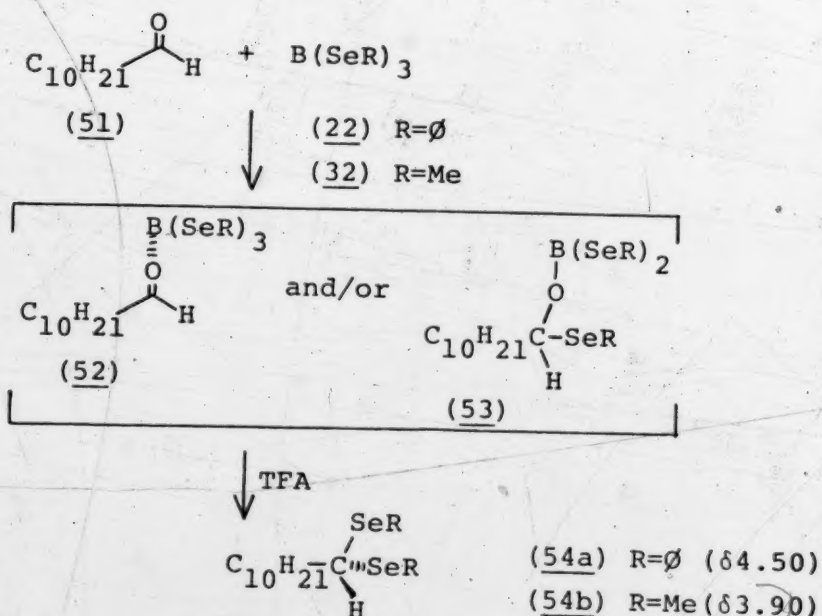
Mechanistic Considerations

During investigations of reagents (22) and (32) for the preparation of selenoacetals, an attempt was made to follow some of the reactions by NMR. We found it convenient to use the signal from the methine proton of undecanal (51) as a probe, because the signals of the various reactants, intermediates, and products are relatively isolated in the spectra even at 60 MHz,

due to large differences in chemical shifts.

The NMR spectra of both reagents (22) and (32) with undecanal (51) without acid show an immediate loss of the aldehydic methine signal at δ 9.7; however, the methine signals due to the selenoacetals (54) do not appear in either case ($R = \text{Me}$ or $R = \emptyset$) until the addition of acid (TFA) to the NMR tube (Scheme VIII). This implies that the reaction of the selenoborane reagents (22) and (32) with (51) is occurring in at least two stages: an initial acid independent reaction

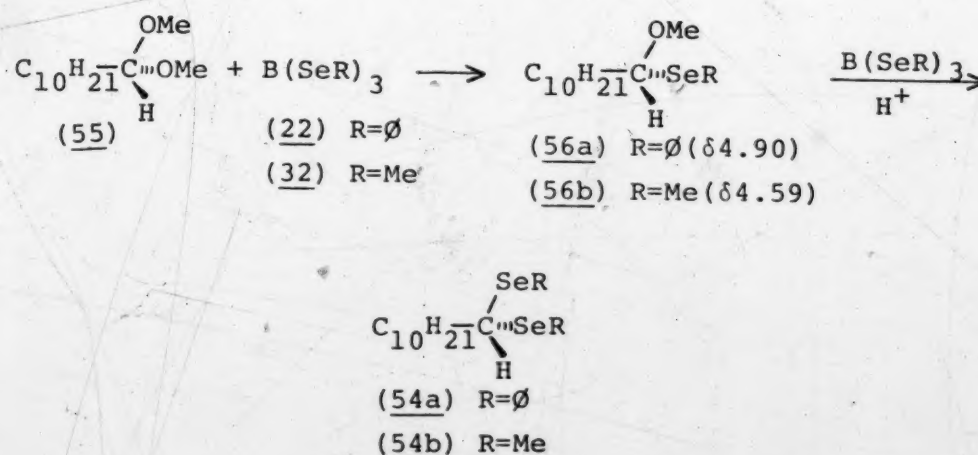
Scheme VIII



to form possibly a Lewis acid complex (52) or an addition compound (53) or both, followed by an acid-induced decomposition of the intermediate(s) into the selenoacetals (54) as shown in Scheme VIII.

While a two step process is only implied from the NMR studies for undecanal (51), we have definite proof that two stages occur for the acetal exchange reaction (eq. (72)). When the phenylselenoborane (22) was mixed with undecanal dimethylacetal (55) in an NMR tube, in the absence of acid we observed the immediate loss of the triplet at δ 4.3 due to the oxygen acetal (55), and the appearance of a new signal (triplet, $J = 6$ Hz) at δ 4.90. This new signal is due to the formation of a stable mixed oxygen-selenium acetal (56a) shown in Scheme IX. The formation of the inter-

Scheme IX



mediate mixed oxygen-selenium acetal species in the absence of acid was found to be a characteristic of the reaction of (22) with dimethyl acetals (eq. (76),



$\text{R} = \emptyset$), and we were able to isolate and completely characterize a few of these compounds from the reaction in equation (76) (Table VIII).

TABLE VIII.

PREPARATION OF MIXED OXYGEN-SELENIUM ACETALS FROM (22)

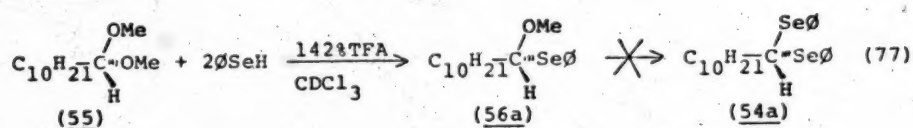
Entry	Acetal	Mixed Acetal	Time	Yield
1	$\text{C}_{10}\text{H}_{21}\text{CH} \begin{array}{l} \text{OMe} \\ \text{OMe} \end{array}$	$\text{C}_{10}\text{H}_{21}\text{CH} \begin{array}{l} \text{Se}\emptyset \\ \text{OMe} \end{array}$	6 h	87%
2			7.5 h	78%
3	$(\text{C}_4\text{H}_9)_2\text{C} \begin{array}{l} \text{OMe} \\ \text{OMe} \end{array}$	$(\text{C}_4\text{H}_9)_2\text{C} \begin{array}{l} \text{Se}\emptyset \\ \text{OMe} \end{array}$	1 h	80%

The reaction of (55) with the methylselenoborane (32) ($\text{R} = \text{Me}$ in eq. (76)) was much slower than the reaction with (22); even after ca. 30 minutes at room temperature, a substantial amount of acetal (55) was still present as judged by the intensity of the methine signal at δ 4.3, while a triplet at δ 4.59 ($\text{J} = 6 \text{ Hz}$)

that we have assigned to the intermediate (56b) was barely detectable. Isolation of the intermediate (56b) was not attempted.

The rate of the acid catalyzed step ((56)→(54), Scheme IX) was observed to be quite sensitive to the structure of the reagent. With phenylselenoborane (22), the conversion of (56a) into selenoacetal (54a) was approximately 70% complete after 10 hours, based on the integrated values of the methine protons of (56a) vs (54a), using 3 mole % TFA (based on acetal (55)); using a large amount of acid (45 mole % TFA), complete conversion of (55) into (54a) was observed after 15 minutes at room temperature. With the methylselenoborane (32) the acceleration of the processes (55)→(56b) and (56b)→(54b) were both noted: using 1.8 mole % TFA (based on (55)) a scan immediately after injection of the acid showed a large triplet at δ 4.59 (presumably (56b)) and a small triplet at δ 3.90 due to (54b); before a full scan and integration could be performed (ca. 5 minutes), the conversion of (56b) to (54b) was complete.

Finally a simple acetal exchange reaction was performed without the presence of boron with two equivalents of benzene selenol and undecanal dimethylacetal (55) (eq. (77)). The following observations were noted: the exchange reaction to form (56a) ((55)→(56a)) does not occur without acid, and is slow

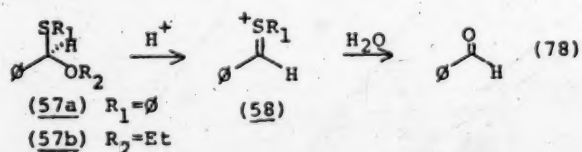


even in the presence of large amounts of acid (ca. 50 mole % based on (55)); the exchange reaction to form the phenylselenoacetal (54a) ((56a)→(54a)) did not occur even in the presence of more than an equivalent of acid (142 mole %).

Conclusions

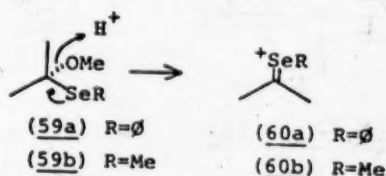
The selenium atom, the boron atom, and the acid all play a distinct role in the exchange reactions (eq. (72)) and, by analogy, the carbonyl deoxygenation reactions (eq. (71) and (74)). Their exact functions cannot be stated without detailed mechanistic studies; however, some reasonable pathway can be suggested.

Jencks has shown that sulfur lone pairs can participate in the hydrolysis of benzaldehyde O,S-acetals⁸⁵ (eq. (78)) with intermediate (58) being favored for



(57b) ($R_1 = \text{Et}$) but not for (57a) ($R_1 = \phi$). The selenium atom lone pairs have been shown to be more available as nucleophiles for methylalkyl selenides

than for phenylalkyl selenides,^{77g} thus conversion of

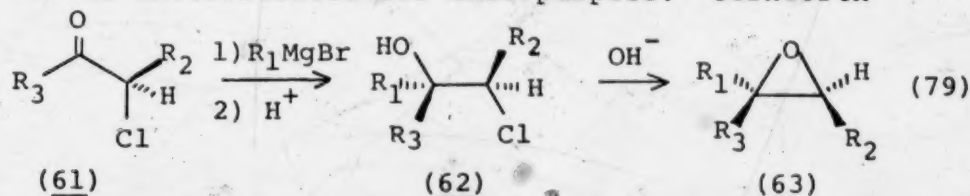


(59b) into a selenium stabilized carbonium ion (60b) is expected to be more favorable than for (59a) and a more rapid acid catalyzed exchange reaction for the methylselenoborane (32) is expected. Using the same argument, the phenylselenoborane (22) should be a stronger Lewis acid than the methylselenoborane (32); consequently, any non-acid catalyzed reactions (exchange to form mixed selenium-oxygen acetals such as (56)) should be slower for (32), and a carbonyl with a low Lewis basicity, such as undecanal⁸⁶ (entry 2, Table VII), is expected to react sluggishly with (32).

It was not the purpose of the present research to make a detailed mechanistic study. The pathway described above is chemically reasonable but evidently represents an oversimplification. In the light of the results from equation (77), it is clear that the boron atom is acting as much more than just a convenient selenol carrier.

DEOXYGENATION OF EPOXIDES

The successful synthesis of many complex organic molecules often hinges on the selective introduction of a carbon-carbon double bond at a specific position, with a known configuration. In recent years, a variety of new reactions have been employed to bring about the introduction of double bonds in a stereospecific or highly stereoselective manner.⁸⁷ Epoxides are potentially very useful intermediates for this purpose. Cornforth^{88a}

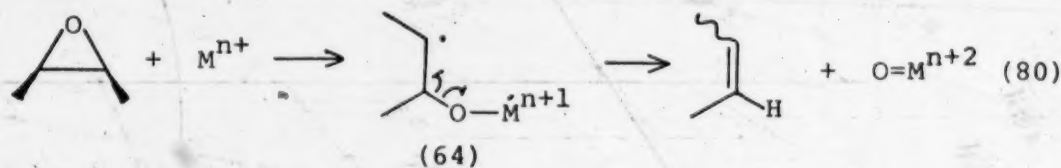


has shown that epoxides may be prepared stereoselectively through the formation of a predominance of one chlorohydrin diastereomer (62) by addition of a Grignard reagent to an α -chloro aldehyde or ketone (61), followed by base treatment of (62) to form epoxide (63) (eq. (79)). The stereoselectivity of the sequence in equation (79) has been improved to over 90% in favor of one diastereomer.^{88b}

Several methods exist for the conversion of epoxides into olefins with varying degrees of stereoselectivity. Multi-step methods, which include stereospecific conversion of the epoxide into an iodohydrin^{88a} or episulfide^{4,89} followed by stereospecific elimination of the inter-

mediates into olefins, will not be reviewed here, except for cases that transitory intermediates are formed and eliminated in situ.

In summary, epoxide deoxygenations may be divided into two broad categories. In one group are those reagents that rely on the formation of an oxygen bond with a low valent transition metal (eq. (80)). This

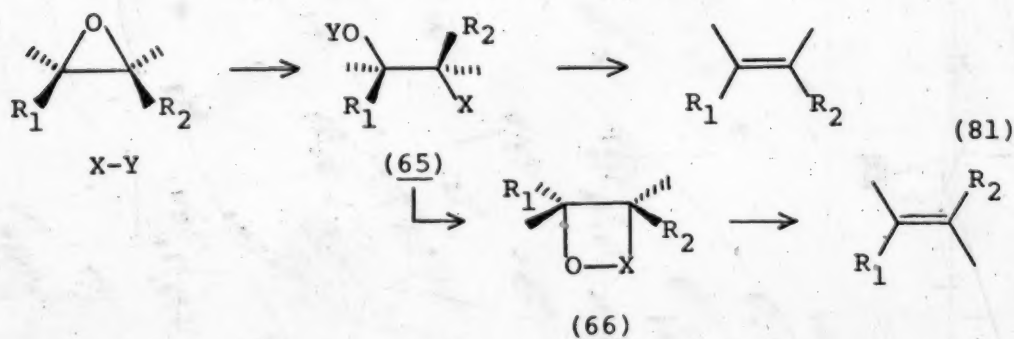


is generally thought to occur through the formation of a carbon radical⁹⁰ such as (64). Free rotation of the carbon radical potentially causes loss of stereochemistry of the starting epoxide, and in most cases these deoxygenations have been found to be non-stereoselective.

A variety of low valent transition metal reagents have been used to deoxygenate epoxides. These include vaporized metal atoms,⁹¹ titanium(II),^{90a} chromium(II)-ethylenediamine complex,^{90b} iron(III)-butyl lithium,^{90c} zinc dust,⁹² zinc-copper couple,⁹³ and reduced cyclopentadienyl complexes of tungsten, molybdenum and titanium.⁹⁴ A mixture of magnesium bromide-magnesium amalgam, shown to give low yields of olefins from epoxides, is thought to proceed through a bromohydrin intermediate.⁹⁵ Tungsten(VI) chloride, reduced to an undefined reagent (possibly tungsten(IV)) with lithium

iodide, was shown to convert trans-epoxides into olefins stereoselectively with retention of configuration, but cis-epoxides gave mixtures of olefinic stereoisomers.⁹⁶ The deoxygenation was thought to go through an iodo-hydrin intermediate, as no stereoselectivity was seen when the tungsten reagent was prepared by butyllithium reduction.⁹⁶

Another group of reagents that convert epoxides into olefins are those that rely on an initial nucleophilic attack on the oxirane ring to form an intermediate addition compound (65); (65) can then undergo an anti-



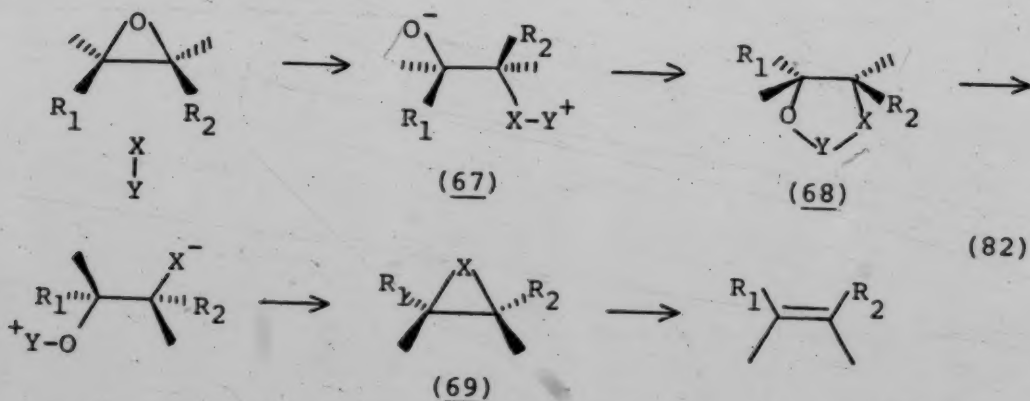
1,2-elimination to form an olefin with retention of the epoxide configuration, or, if the nucleophile, X, can form a strong bond with oxygen, the intermediate (66) may form followed by a syn-1,2-elimination resulting in an olefin with inverted configuration (eq. (81)). A high degree of stereoselectivity is normally associated with these types of processes.

Reagents that stereospecifically convert epoxides into olefins with retention of configuration (anti-elimination) include treatment of the epoxide with iodide ion ($X = I$) followed by addition of phosphoryl chloride ($Y = P(O)Cl_2$)-pyridine;⁹⁷ methyltriphenoxyposphonium iodide ($X = I$, $Y = (O)_3PMe$) in the presence of boron trifluoride etherate, which gives high yields of olefins except for terminal epoxides;⁹⁸ and addition of sodium (cyclopentadienyl)dicarbonylferrate ($X = CpFe(CO)_2$) followed by tetrafluoroboric acid ($Y = H$).⁹⁹ Diphenylphosphorus tetraiodide has recently been reported to efficiently convert epoxides into olefins in the presence of sensitive functional groups,¹⁰⁰ but the stereoselectivity was not investigated.

Since olefins are readily converted into epoxides with retention of stereochemistry by treatment with m-chloroperbenzoic acid,¹⁰¹ stereospecific conversion of epoxides into olefins with inversion of configuration (eq. (81)) constitutes a method for inverting olefin stereochemistry.¹⁰² Several procedures have been reported recently for this type of reaction, but all are dependent on an initial nucleophilic ring opening and subsequent rotation to form a four-membered intermediate (66) reminiscent of a Wittig reaction; in fact, phosphites^{103a} and phosphines^{103b} were shown to convert epoxides into olefins with inversion of stereochemistry,

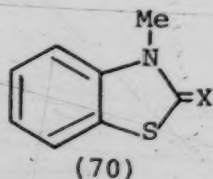
although stereoselectivity was low and extreme conditions were required. Excellent stereospecificity has been reported from the use of: sodium (cyclopentadienyl)-dicarbonylferrate ($X = \text{CpFe}(\text{CO})_2$) followed by pyrolysis (130°) of the adduct (66);¹⁰⁴ trialkylsilyl anions¹⁰⁵ in HMPA^{105a} ($X = \text{R}_3\text{Si}$); and lithium diphenylphosphide followed by methyl iodide ($X = \phi_2(\text{Me})\text{P}$)¹⁰⁶ which was shown to convert (*Z*)-1,2-epoxycyclooctane into (*E*)-cyclooctene without contamination by the (*Z*)-isomer.^{106a} Octacarbonyldicobalt has been shown to convert epoxides into olefins with inversion of stereochemistry,¹⁰⁷ but the epoxide requires one or more electron withdrawing groups for a successful reaction.

A third type of epoxide deoxygenation is based on nucleophilic oxirane ring opening as summarized in equation (82). The overall process involves an initial



nucleophilic attack to form an activated Y moiety (as in (67)), which bonds to the oxygen anion forming an unstable

intermediate (68) subsequent to rotation about the carbon-carbon bond. Cleavage of the X-Y bond of intermediate (68) followed by another rotation and then a backside attack results in the cyclic three-membered product (69) with a net retention of configuration. This type of process has been shown to effect the stereospecific conversion of epoxides into episulfides, with retention of stereochemistry, using tributylphosphine sulfide⁴ and 3-methylbenzothiazole-2-thione⁸⁹ (70), X = S). The



conversion of epoxides into olefins by this method requires the stereospecific extrusion of X in intermediate (69) which, for episulfides, needs rather vigorous conditions.¹⁰⁸ However, episelenides (X = Se in eq. (82)) had been shown to be unstable to olefin formation,^{109,110} and the consequent use of selenium methodology has resulted in three stereospecific epoxide deoxygenation reagents based on the process represented in equation (82): triphenylphosphine selenide² and 3-methylbenzothiazole-2-selenone ((70), X = Se)^{111a} with trifluoroacetic acid, and potassium selenocyanate^{111b} in methanol.

These reagents do not convert epoxycyclopentanes into cyclopentene. It has been proposed^{111b} that this is due to the strain¹¹² that would be involved during

the formation of a trans-fused [5,5] bicyclic intermediate analogous to (68).

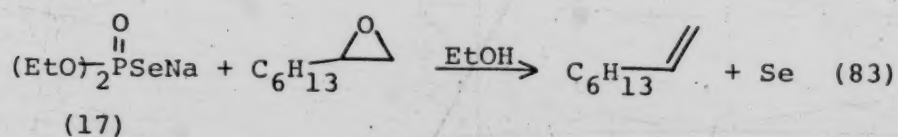
That episelenide ((69), X = Se) intermediates are involved in the deoxygenation of epoxides with phosphine selenides has been shown spectroscopically,¹¹³ although the episelenides proved to be too unstable for isolation.

The Phosphorus-Tellurium Reagent

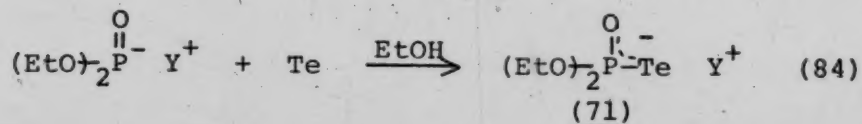
In the wake of the highly productive area¹¹⁴ that has developed since the first modern organic transformation was performed based on selenium chemistry,² much effort has been put into the possible development of tellurium methodology.¹¹⁵ These studies have provided two new methods for the generally easy process of converting vicinal dibromides into olefins, using diphenyl telluride¹¹⁶ and sodium telluride.¹¹⁷ One investigator in the selenium and tellurium fields has stated "[The] general tendency toward greater reactivity with the organo-selenium analogs of sulfur species suggests that other new selenium reagents are likely to be found which offer advantages over their sulfur counterparts. By contrast we have found nothing to suggest that the development of tellurium reagents is likely to be a fruitful endeavor."¹¹⁸

Results and Discussion

During our investigation of the chemistry of sodium O,O-diethyl phosphoroselenoate (17), we looked at the possibility of using (17) to convert epoxides into olefins, anticipating a process similar to equation (82). While we noted that (17) did convert terminal epoxides into olefins (eq. (83)), the reaction proceeded quite



slowly. An attempt was made to prepare and isolate the analogous sodium telluroate (71) according to equation (84) ($\text{Y} = \text{Na}$), but the resulting solution was so sensitive



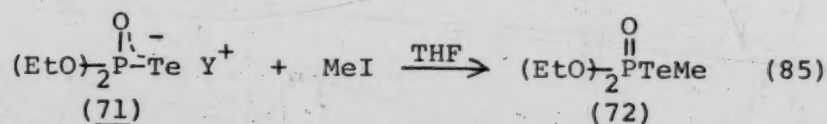
to air that no product could be isolated without extensive contamination by metallic tellurium. However, the analogous potassium salt of (71) had been reportedly prepared by the same method,¹¹⁹ and we felt that (71) could be generated in situ.

Far less than a stoichiometric amount of tellurium would dissolve in an ethanolic solution of sodium O,O-diethyl phosphite, possibly due to an unfavorable equilibrium of ethanolic sodium diethyl phosphite, which has been shown to be predominately protonated in

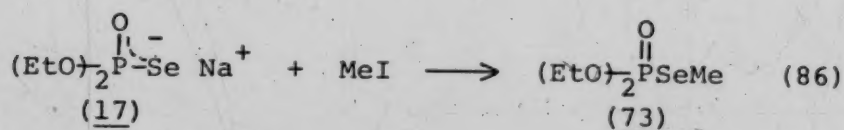
ethanol.¹²⁰ However, if the sodium phosphite was prepared in THF, stoichiometric amounts of tellurium powder would dissolve quickly to form a colorless solution.

Evaporation of the solvent with rigorous exclusion of air yielded a white crystalline solid, which immediately turned black in the presence of oxygen.

Addition of methyl iodide to a THF solution of (71) ($Y = Na$) produced an unstable product (72) (eq. (85)) that gradually precipitated tellurium metal. The



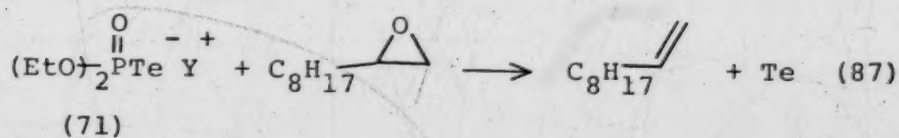
NMR spectrum (d_8 -THF) of the solution immediately after the addition of methyl iodide showed an intense doublet at δ 1.87 ($J = 12.2$ Hz); this signal was attributed to the methyl ester (72) by analogy with the reaction of the selenium salt (17) with methyl iodide (eq. (86)) to give methyl ester (73). The latter shows a doublet at δ 2.1



($J = 13$ Hz), and the salt (17) is known to be alkylated only on the selenium atom with alkyl halides.¹²¹

All of our early epoxide deoxygenations were done in ethanolic sodium phosphite solutions, which would only dissolve small quantities of tellurium metal.

We observed that the reaction of (71) with epoxides deposited tellurium metal along with olefin (eq. (87)); therefore, it seemed reasonable to assume that the



reaction responsible for initial dissolution of the tellurium metal (eq. (84)) would also dissolve any tellurium produced via equation (87), and thus the deoxygenation of epoxides with phosphite anion and tellurium metal should be catalytic with respect to tellurium. This was found to be the case: a suspension of ethanolic sodium O,O-diethyl phosphite and a small amount of tellurium metal was stirred until a clear solution resulted; addition of a nearly stoichiometric quantity (based on phosphite) of terminal epoxide caused a small release of heat and the precipitation of tellurium after a few minutes to several hours, depending on the initial amount of tellurium added. Analysis of the reaction mixture by vapor phase chromatography (VPC) showed that the epoxide had been efficiently converted into olefin. That the reactive species was (71) was inferred from the observation that mixtures of sodium O,O-diethyl phosphite in ethanol, sodium ethoxide and tellurium metal in ethanol, and hydrogen O,O-diethyl phosphite and tellurium metal in ethanol were all inert to terminal

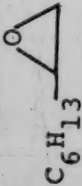
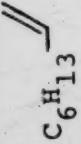
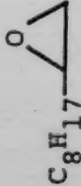
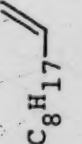
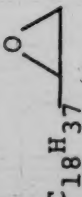
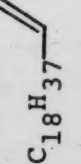
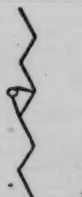
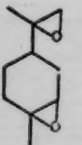
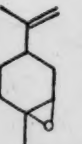
epoxides under similar conditions (as judged by VPC).

The interesting observation was made that due to the rapid reaction of the phosphite with tellurium metal, a suspension of the epoxide and tellurium metal could be prepared followed by portionwise addition of the phosphite reactant. As long as much larger than stoichiometric amounts (based on tellurium) of phosphite were added in each portion, a colorless solution was obtained until nearly all the phosphite from the addition was consumed, at which stage tellurium metal rapidly precipitated. A further portion of phosphite could then be added which caused immediate dissolution of the tellurium. This procedure was repeated until all the epoxide had been converted into olefin.

The deoxygenation was performed on a variety of epoxides, and the results are summarized in Table IX.

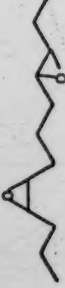
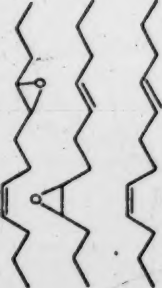
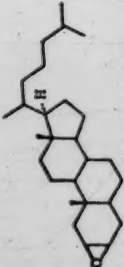
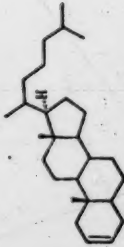
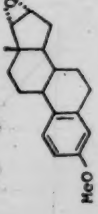
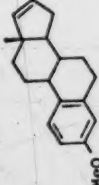
Using the procedure described above, high yields of olefins were isolated from terminal epoxides (entries 1, 2, 3). However, attempts to deoxygenate internal epoxides resulted in very low conversions (entry 4), or required a prolonged reaction time (entry 6). Competition experiments confirmed the implication that terminal epoxides may be selectively deoxygenated in the presence of an internal epoxide: the catalytic deoxygenation by the tellurium reagent (71) of equimolar amounts of 1,2-epoxydecane and 1,2-epoxycyclohexane produced an

TABLE IX. DEOXYGENATION OF EPOXIDES

Entry	Epoxide	T _e (eq.)	Phosphite (eq.)	Time (h)	Temp.	Product	% Yield
1	 C ₆ H ₁₀ O	0.02	1.13	24	R.T.	 C ₆ H ₁₂	72
2	 C ₈ H ₁₄ O	0.25	1.42	26	R.T.	 C ₈ H ₁₆	70
3	 C ₁₄ H ₂₆ O	0.15	1.67	12	R.T.	 C ₁₆ H ₃₂	91
4	 C ₁₄ H ₂₆ O	0.19	1.15	13	R.T.	 C ₁₆ H ₃₂	< 1 ^a > 97 ^a
5	 C ₆ H ₁₀ O	0.07	2.0	18.5	R.T.	 C ₇ H ₁₂	76 ^a
6	 C ₆ H ₁₀ O	0.23	1.17	42	R.T.	 C ₆ H ₁₀	88 ^a

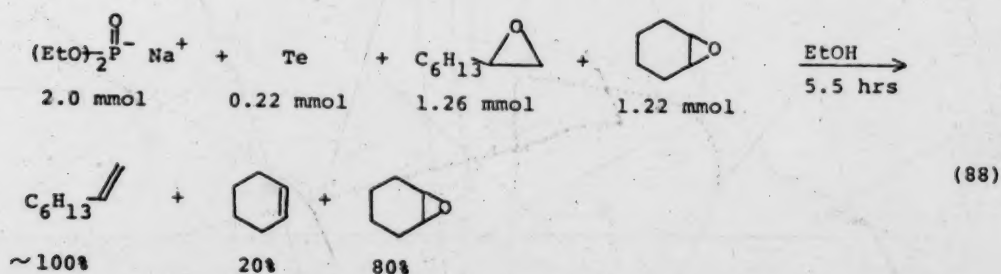
(continued)

TABLE IX (continued)

Entry	Epoxide	T _e (eq.)	Phosphite (eq.)	Time (h)	Temp.	Product	% Yield
7		1.02	1.04	2	80		76.7 ^a 16.5 ^a
8		1.1	1.0	19	80		46.6 ^a 27.9 ^a
9		1.1	1.1	17	80		46.8 5.7 6.6
10		1.0	1.1	5.5	80		90
11		2.67	3.17	46	80		39

^aYield determined by VPC with internal standard.

almost quantitative yield of 1-decene, while most of the epoxycyclohexane still remained (eq. (88)) (as



judged by VPC with an internal standard). This selectivity was further shown by the partial deoxygenation of limonene diepoxide (entry 5).

Since the catalytic method proved to be unsatisfactory for the deoxygenation of internal epoxides, an alternate procedure was developed for the preparation of stoichiometric quantities of (71). The metallated O,O-diethyl phosphite, prepared in anhydrous THF, was injected into a flask containing an equivalent amount of tellurium powder. The tellurium slowly dissolved (ca. 1-2 h) to give a colorless solution. Unfortunately the THF solution of (71) did not possess the ability to deoxygenate epoxides; however, if the solvent was first evaporated (with exclusion of air) followed by the addition of dried ethanol, the resulting colorless solution proved to be a powerful epoxide deoxygenator.

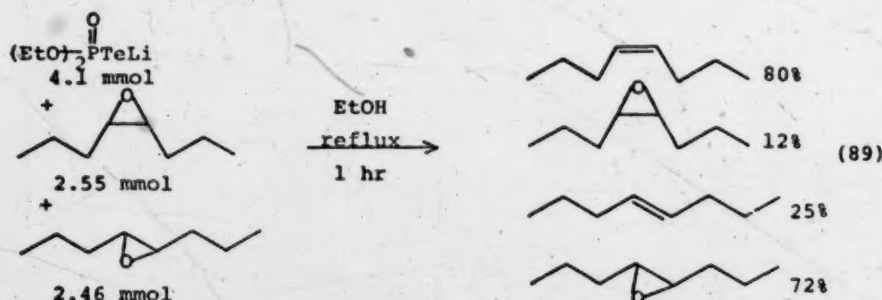
In this manner, the potassium, sodium, and lithium salts of (71) were prepared. A qualitative examination

of the relative rates of the different salts of (71) on the deoxygenation of 1,2-epoxycyclohexane and (Z)-4,5-epoxyoctane showed that the reaction of the lithium salt occurred much faster than the other two. For this reason, the lithium salt of (71) was used for the deoxygenation of all internal epoxides.

From Table IX, it can be seen that even with stoichiometric amounts of tellurium, the deoxygenations still required the reflux temperature of ethanol for internal epoxides. The deoxygenations were shown to be stereospecific with retention of configuration: (Z)-epoxide (entry 7) gave (Z)-olefin, and (E)-epoxide (entry 8) gave (E) olefin. It is also noted that the deoxygenation works very well for epoxycyclohexanes (entry 10), while epoxycyclopentanes (entry 11) are quite slow and do not react satisfactorily.

The apparent inefficiency of the lithium reagent (71) to deoxygenate (E)-epoxides (entry 8) relative to (Z)-epoxides (entries 7 and 10) generated interest in the possibility of a further form of selectivity peculiar to (71): namely the ability to deoxygenate (Z)-epoxides in the presence of the (E)-isomers. A preliminary experiment readily confirmed this. When equivalent amounts of (E)- and (Z)-epoxyoctanes were mixed with the lithium reagent (71), the (Z)-epoxide was converted into (Z)-olefin much faster than the (E)-isomer (as judged by

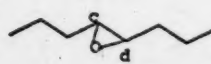
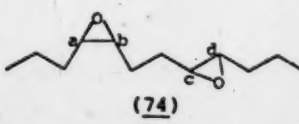
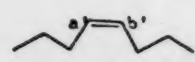
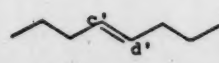
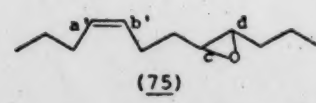
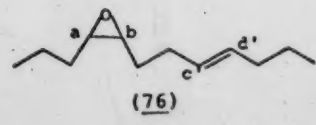
VPC with an internal standard) (eq. (89)).



This selectivity was tested further by treating a molecule containing both (E)- and (Z)-epoxides with (71). (4E,8Z)-4,5,8,9-Diepoxydodecane (74) was deoxygenated with one equivalent of the lithium salt of (71) (entry 9). Chromatography of the reaction mixture led to the isolation of a major product and a minor one. The minor product (6.6% yield) was spectroscopically identical to (4E,8Z)-dodecadiene. Silver nitrate impregnated silica gel TLC showed the major product to be a mixture of two closely-running compounds: a lower R_f major component and a higher R_f minor component.

Identification of the mixture was greatly simplified from the published report that (Z)- and (E)-olefins are readily distinguishable by ^{13}C NMR,¹²² and our own observations that (Z)- and (E)-epoxides have characteristic chemical shifts in ^{13}C and proton NMR (Table X). It can be seen that (Z)-olefins come slightly upfield from (E)-olefins (entries 4 and 5) and (E)-epoxides come downfield from (Z)-epoxides (entries 1 and 2) in ^{13}C NMR,

TABLE X. NMR SHIFT DATA FOR (E)- AND (Z)-EPOXIDES
AND OLEFINS

Entry	Compound	δ C	δ H
1		$a = b = 57.0$	$a = b = 2.8$
2		$c = d = 58.7$	$c = d = 2.65$
3		$a, b = 57.2, 57.1, 56.7, 56.4$ $c, d = 58.9, 58.7, 58.3, 58.0$	$a = b = 2.95$ $c = d = 2.65$
4		$a' = b' = 130.0$	
5		$c' = d' = 130.5$	
6a		$a', b' = 130.6, 128.6$ $c, d = 58.7, 58.3$	$c, d = 2.68$
b		$c', d' = 131.2, 129.2$ $a, b = 57.0, 56.6$	$a, b = 2.92$

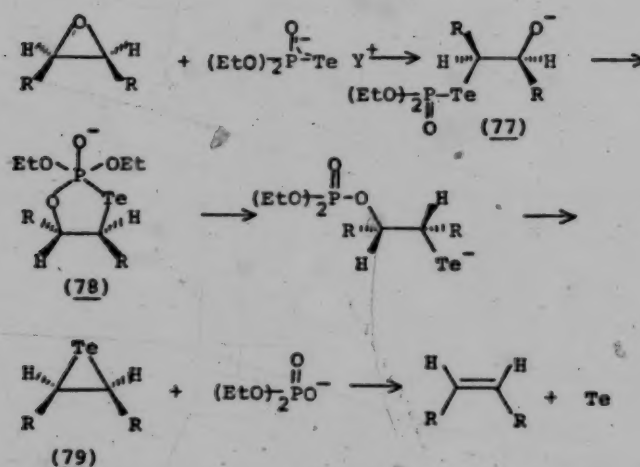
while (Z)-epoxides come downfield from (E)-epoxides (entries 1 and 2) by proton NMR. The power of ^{13}C NMR to distinguish epoxide isomers is seen for the diepoxide (entry 3) which is clearly shown to be the expected mixture of diastereomers.

A ^{13}C NMR spectrum of the major product from the deoxygenation of (74) (entries 6a and 6b) showed twelve large signals, two in the olefinic region (δ : 130.6 and 128.6) and two in the epoxide region (δ : 58.7 and 58.3); associated with these signals were twelve small signals, two slightly downfield from the major olefinic signals (δ : 131.2 and 129.2) and two upfield from the major signals in the epoxide region. This clearly shows that the major product from the deoxygenation of diepoxide (74) is a mixture of two isomers, the major component being (4E,8Z)-4,5-epoxydodec-8-ene (75) and the minor component being the isomeric (4Z,8E)-4,5-epoxydodec-8-ene (76). This was confirmed by proton NMR, which showed a major signal at δ 2.68 ((E)-epoxide) and a minor signal at δ 2.92 ((Z)-epoxide) along with the other signals compatible with the product. A 400 MHz proton spectrum showed excellent baseline separation of the epoxide signals, and integration of the signals showed the isomers to be present in a ratio of 8.2:1.

Mechanistic Considerations

A chemically reasonable process depicting the course of epoxide deoxygenation with (71), based on the process shown in equation (82) which has been proposed for the stereospecific deoxygenation of epoxides with triphenylphosphine selenide,^{2,113} is shown in Scheme X.

Scheme X



An initial nucleophilic stage to form the intermediate (77) is consistent with the enhanced reactivity of terminal epoxides over other types; and the greater facility for the deoxygenation of (Z)-epoxides as compared with (E)-isomers is the same kind of behavior observed in the reduction of isomeric epoxides by lithium aluminum hydride.¹²³ Formation of a cyclic intermediate (78) accounts for the slowness of reactions involving epoxy-cyclopentanes (entry 11)¹²⁴ because for these compounds

such an intermediate (trans-fused [5.5] bicycle) is geometrically unfavorable.¹¹² The epitelluride (79) proposed is a compound class that has been detected spectroscopically.¹²⁵ Finally, in accordance with Scheme X, one of the products of the deoxygenation reaction is diethyl phosphate, which we have isolated as diethylphosphoric acid and identified by spectroscopic (IR and NMR) comparison with an authentic sample.

EXPERIMENTAL

All solvents for reactions, extraction, or chromatography were distilled before use. Dry solvents were distilled (under vacuum where applicable) under a static nitrogen atmosphere over suitable desiccants and transferred via oven-dried syringes. Dry carbon disulfide, chloroform, and deuterated chloroform were distilled from phosphorus pentoxide; toluene, dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), and dichloromethane from calcium hydride; benzene, pentane, and hexane from lithium aluminum hydride; diethyl ether, tetrahydrofuran (THF), and hexamethylphosphoramide (HMPA) from sodium. Ethanol was dried by the Lund-Bjerrum method.

Dry nitrogen refers to nitrogen purified by passage through a column (3.5 x 42 cm) of R-311 catalyst¹²⁶ and through a similar column of Drierite.

For reactions done under dry nitrogen, oven dried (> 3 h at 120°) glassware was used. The apparatus was assembled hot and (where applicable) capped with a rubber septum. Nitrogen inlet and exit needles were then placed in the septum and the flask purged until cool (ca. 20 min). Reactions were performed after removal of the exit needle, unless gas was being generated. The same procedure was employed if a flask was used to contain a material prior to addition of that material to another flask used for the reaction.

All vapor phase chromatography (VPC) analyses were performed on a Hewlett-Packard 5830A gas chromatograph equipped with an FID detector and, unless otherwise noted, with prepacked Hewlett-Packard 6 ft, 1/8 in OD stainless steel analytical columns with nitrogen as the carrier gas. Yields were evaluated in the following manner by VPC: a standard solution was prepared composed of the compounds to be analyzed plus an inert internal standard diluted with the appropriate solvent to the approximate concentration expected to occur from the reaction. Response factors¹²⁷ of each component, compared to the internal standard, were calculated. The absolute yield of a specific component was then readily calculated by addition of a known amount of internal standard (close to that of the standard solution) to a quenched solution of reaction mixture, followed by VPC analysis. Response factors and yields were based on a minimum of three injections.

Alumina for preparative (PLC) and thin layer chromatography (TLC) was Merck type GF-254 (type 60/E), and silica gel was Merck type 60-PF-254; plates for preparative layer chromatography were 60 x 20 x 0.1 cm and were heated for 2 h at 110° before use. Silver nitrate plates were prepared on the basis of weight silver nitrate per weight silica or alumina. UV active spots were detected at 254 nm; spots detected by spraying with H₂SO₄ (50% in methanol) were charred on a hot plate.

Alumina for column chromatography was Camag neutral aluminum oxide of Brockmann activity three; silica gel was Merck type 60, 70-230 mesh ASTM.

Infrared spectra were recorded on a Perkin-Elmer 297 infrared spectrophotometer; liquids and oils were run as neat films on sodium chloride plates, solids were run as solutions (solvent specified) in 0.5 mm sodium chloride cells. Proton NMR spectra were recorded on a Varian HA 100 spectrometer with TMS as an internal standard. ¹³C NMR spectra were recorded on a Bruker HFX-90 or WP-60 spectrometer with deuterated chloroform as an internal standard. Mass spectra were recorded on an A.E.I. MS-50 mass spectrometer at an ionizing voltage of 70 eV..

For reactions run at 0°, the reaction flasks were cooled in an ice-water bath; at -30°, in a slush composed of 2:1 H₂O-methanol and dry-ice; at -60 to -70°, in a dry-ice, ethanol bath.

Unless otherwise noted, stirring refers to the use of a teflon coated magnetic stir bar.

All weights of solid and non-distillable liquid products were recorded after a minimum of 2 h oil pump evacuation at < 0.1 mm with a liquid nitrogen trap.

Evaporation of solvent refers to the use of a rotary evaporator with a water pump vacuum and room temperature water bath.

Tris(phenylseleno)borane (22) was always transferred

into a septum covered pre-weighed flask inside a glove bag filled with dry nitrogen.

Melting points were determined on a Kofler block melting point apparatus. Boiling points quoted for products distilled in a Kugelrohr apparatus refer to oven temperature.

Deoxygenation of Sulfoxides

O,O-Diethyl Hydrogenphosphoroselenoate⁵⁸ (13)

Sodium O,O-diethyl phosphoroselenoate (17)⁵⁹ (mp 195.0-195.5°) (2.00 g, 8.37 mmol) was dissolved in water (40 mL) and acidified with HCl (2 mL) in a separatory funnel. The dense oil that separated was taken into ether (2 x 40 mL portions); the ether layers were combined, dried (Na_2SO_4), filtered and the solvent evaporated. The concentrate was taken into methylene chloride (30 mL), dried (MgSO_4), filtered and the solvent evaporated. The residue was evacuated (< 0.1 mm) for 0.5 h yielding 1.62 g of (89%) as a pale yellow oil; NMR (CDCl_3) δ 1.36 (t, J = 7 Hz, 6H), 4.04 and 4.21 (overlapping q, J = 8 Hz, 4H), 6.22 (s, 1H).

Bis (O,O diethyl phosphoryl)diselenide⁵⁹ (18)

This compound was prepared exactly according to the literature, from the sodium salt (17), in 85% yield as a

bright yellow-orange oil; NMR (CDCl_3) δ 1.40 and 1.41 (overlapping t, $J = 7$ Hz, 6H), 4.20 and 4.35 (overlapping q, $J = 7$ Hz, 4H).

Reaction of (13) with DMSO (entry 1, Table II)

(a) Equimolar amounts of freshly prepared acid (13) (0.139 g, 0.643 mmol) and DMSO (0.0493 g, 0.632 mmol) were placed in an NMR tube with ca. 0.5 mL CDCl_3 . The bright yellow turbid solution was allowed to stand overnight. Integration of the signals due to DMSO (δ 2.69) and Me_2S (δ 2.09) from a 60 MHz NMR spectrum showed the ratio (DMSO/ Me_2S) to be 1.23:1.

(b) Two equivalents of acid (17) (0.549 g, 2.53 mmol) and one equivalent of DMSO (0.0986 g, 1.26 mmol) were placed in an NMR tube with ca. 1 mL CDCl_3 , yielding a bright yellow turbid solution. After 1 h at room temperature, the 60 MHz NMR spectrum showed a Me_2S /DMSO ratio of 38.7:1 (97.5% conversion).

Reaction of (18) with DMSO

Freshly prepared diselenide (18) (1.75 g, 4.05 mmol) and DMSO (0.63 g, 8.08 mmol) were combined and allowed to stand overnight, resulting in a black precipitate. The suspension was diluted with CDCl_3 and filtered into an NMR tube. A 60 MHz NMR spectrum showed the ratio of DMSO



(s, δ 2.68) to Me_2S (s, δ 2.05) to be 3.71:1.

Reduction of 1,1'-sulfinylbisbutane with (13) (entry 2,
Table II)

The sulfoxide¹²⁸ (16.44 g, 101.3 mmol) was dissolved in dry pentane (300 mL) in a flask equipped with an addition funnel and a paddle stirrer under a dry nitrogen atmosphere. The acid (13), freshly prepared from the sodium salt (17) (53.42 g, 223.5 mmol) and HCl (50 mL), was dissolved in dry methylene chloride (10 mL), transferred to the addition funnel via syringe, and diluted with dry pentane (100 mL). The acid was added over a 10 min period with stirring under dry nitrogen, and stirring continued for 2 h, resulting in two layers. The dark yellow-orange layer was separated, washed once with pentane (100 mL), and the pentane combined with the yellow upper layer. The resulting solution was diluted with ether (100 mL), washed three times with 0.2 M K_2CO_3 (200 mL portions), dried (Na_2SO_4), filtered and concentrated to ca. 70 mL by distillation through a 1 x 25 cm column packed with glass helices; the remainder of solvent was removed by distillation through a 1 x 20 cm vigreux column. The residue was treated with decolorizing carbon (1 x 5 cm column, pentane elution), the solvent removed through a 1 x 25 cm vigreux column, and the sulfide collected as a colorless liquid (12.35 g, 83.3%) at 128-132° (150 mm).

The product was 99% pure by VPC¹²⁹ and had identical VPC retention time, b.p., IR, and NMR to authentic di-n-butyl sulfide.

Reduction of dibenzyl sulfoxide with (13) [entry 3, Table II]

The sulfoxide¹³⁰ (1.7845 g, 7.755 mmol) was placed in a flask (50 mL) under a dry nitrogen atmosphere. The acid (13), freshly prepared from the sodium salt (17) (3.95 g, 16.5 mmol) and HCl (4 mL), was dissolved in dry CH₂Cl₂ (10 mL) and added in one portion via syringe to the flask. The solution was stirred 1 h at room temperature and an additional portion of acid (13), prepared from the sodium salt (2.00 g, 8.37 mmol), was added to the reaction mixture with dry CH₂Cl₂ (10 mL). After stirring an additional 2 h, the solvent was removed, and the residue filtered through an alumina column (1.5 x 20 cm) with pentane elution. After evaporation of the eluate, the residue was chromatographed on an activity I alumina column (3 x 35 cm) with CH₂Cl₂ elution. Evaporation of solvent from fractions containing dibenzyl sulfide yielded a pale yellow crystalline residue. Vacuum sublimation (ca. 1 μ , 40° oil bath) yielded a white crystalline solid (1.5320 g, 92.3%), mp 49-50°. The product had identical TLC (alumina, pentane), mp, IR, and NMR to authentic dibenzyl sulfide.

Reduction of diphenyl sulfoxide with (13) (entry 4,

Table II)

The sulfoxide¹³¹ (2.8347 g, 14.02 mmol) was placed in a flask (50 mL) equipped with a reflux condenser, under a dry nitrogen atmosphere. The acid (13), prepared freshly before each addition and added in three approximately equal portions over a 25 h period, was obtained from the sodium salt (17) (14.51 g, 60.7 mmol) and dissolved in dry CH_2Cl_2 (total volume, 24 mL). Reflux was continued throughout the additions, and for 3.5 h after the last addition. The solvent was evaporated from the reaction mixture and the bright yellow residue filtered thorough an alumina column (1 x 23 cm) with pentane elution. The eluate was removed, and the residue was chromatographed on activity I alumina (3 x 35 cm column) with benzene elution. Fractions containing diphenyl sulfide were combined and the solvent evaporated. The colorless liquid was diluted with pentane and evaporated; this was repeated 3 times, finally yielding a colorless liquid (2.4589 g, 94.2%) that was homogeneous by VPC¹³² (99.34%) and TLC (silica gel, pentane). Retention time, R_f , IR, and NMR were identical to authentic diphenyl sulfide.

Reduction of 2-methyl-2-(methylsulfinyl)propane with (13)
(entry 7, Table II)

The sulfoxide¹³³ (0.5160 g, 4.30 mmol) was placed

in a flask (25 mL) equipped with a reflux condenser under a dry nitrogen atmosphere. The acid (13) (8.15 g, 24.7 mmol) freshly prepared before each addition and added in three approximately equal portions over a 13 h period, was injected in a total volume of 18 mL dry CH_2Cl_2 . Reflux was continued throughout the additions, and for a further 12 h after the last addition. The total product was then filtered through an alumina column (2 x 30 cm), the solvent removed by slow distillation through a 1 x 25 cm vigreux column, and octane (0.1444 g) added to the residue as an internal standard. VPC¹³⁴ analysis of the residue (ca. 50 mL) when compared to a VPC of a standard solution composed of 0.1544 g octane and 0.1689 g authentic sulfide in 50 mL CH_2Cl_2 , showed the yield of sulfide to be 80%; VPC retention time and NMR of the residue were identical to authentic methyl t-butyl sulfide.

Reduction of 2,2'-sulfinylbis(2-methylpropane) with (13)
(entry 8, Table II)

The sulfoxide¹³⁵ (0.1161 g, 0.715 mmol) was placed in a flask (10 mL) equipped with a reflux condenser under a dry nitrogen atmosphere. The freshly prepared acid (13) (0.6545 g, 3.02 mmol) was dissolved in dry CHCl_3 (3 mL) and added to the reaction flask via syringe. After 14 h reflux, the total product was filtered through an alumina column (1.5 x 20 cm) with CH_2Cl_2 elution. The

solvent was removed by slow distillation through a vigreux column (3 x 40 cm). To the residue (ca. 1 mL) was added methyl t-butyl sulfide (20.0 mg) as an internal standard. VPC¹³⁶ analysis of the residue, when compared to a VPC of a standard solution composed of 80 mg di-t-butyl sulfide and 76.5 mg methyl t-butyl sulfide diluted to 1 mL with CH₂Cl₂, showed the yield of di-t-butyl sulfide to be 13%. The product was not characterized, aside from the retention time of the VPC trace.

Reduction of 4-(methylsulfinyl)toluene (entry 5, Table II)
and tetramethylene sulfoxide (entry 6, Table II)

These reductions were performed as described in Table II by Dr. Chi Kowk Wong and William A. Kiele, respectively.

Tris(phenylseleno)borane^{62a} (22)

Passage of nitrogen was continued throughout the experiment. Boron tribromide (14.32 g, 57.1 mmol) was placed in a 250-mL three-necked flask equipped with a pressure-equalizing addition funnel, a magnetic stirring bar and a double-walled condenser closed with a rubber septum under a dry nitrogen atmosphere. The flask was cooled in an ice bath and the stirrer was started. Dry carbon disulfide (100 mL) was injected into the flask and

a solution of benzeneselenol¹³⁷ (26.95 g, 17.16 mmol) in dry CS_2 (50 mL) was added from the addition funnel over a four hour period. The ice bath, and hence the solution, were then allowed to warm to room temperature and stirring was continued overnight. The septum on the condenser was replaced by a vacuum takeoff with tap which was connected in series to a large trap cooled in dry-ice-ethanol, a tube packed with anhydrous calcium sulfate, and a water pump. Passage of nitrogen was stopped and the solvent was evaporated. The residual yellow solid was suspended in dry pentane (100 mL) and the stirred mixture was refluxed for 4 h under a slight static pressure of nitrogen. The mixture was cooled slightly and the yellow supernatant was removed by syringe. This procedure was repeated with two more portions (each 100 mL) of pentane. The resulting off-white solid was dried under vacuum. The material weighed 20.48 g (74%). It was sealed in ampoules for prolonged storage.

Dimethyl diselenide¹³⁸ (33)

This compound was prepared in a fume hood. Selenium powder (27.39 g, 347 mmol) and NaBH_4 (9.13 g, 242 mmol) were placed in a 1-L flask equipped with a magnetic stirring bar, a pressure-equalizing addition funnel charged with dry ethanol (500 mL), and a double-

walled condenser closed with a septum. The latter carried inlet and exit needles for nitrogen. The ethanol was added over 2 h, with stirring, to the Se-NaBH₄ mixture. Ice-bath cooling was required to control the resulting vigorous reaction. The mixture was refluxed for 1.5 h and was then cooled to ~ 0°C. MeI (55.0 g, 387.5 mmol) was added in one portion with stirring, and stirring was continued overnight. The mixture was partitioned between water (300 mL) and pentane (200 mL). The dark yellow pentane layer was washed with water (2 x 1 L). The initial aqueous phase (containing most of both the ethanol and the 300-mL portion of water) was extracted with pentane (300 mL) and this organic extract was washed once with water (200 mL). The pentane layers were combined and dried and dimethyl diselenide (15.62 g, 47%) was isolated by distillation as a bright yellow liquid suitable for the next stage: b.p. 55-60° (~ 50 mm).

Tris(methylseleno)borane^{62b} (32)

This compound was prepared under a slight static pressure of nitrogen. Dimethyl diselenide (15.62 g, 83 mmol) was added to commercial dry Et₂O (200 mL) contained in a 500 mL flask carrying a double-walled condenser fitted with a septum (which was used for introduction of nitrogen). The ether solution was stirred magnetically and cooled to about -80° by a dry ice-acetone bath.

LiAlH_4 (1.80 g, 47.5 mmol) was added in one portion and the mixture was stirred for 72 h, the cold bath being allowed to attain room temperature during the first 2-3 h. After the 3-day period $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (8.40 g, 59.2 mmol) was injected through the septum at the top of the condenser and the suspension was refluxed with stirring for 6 h. The mixture was cooled and volatile material was evaporated at room temperature using an oil pump and a large trap cooled by liquid nitrogen. The residual grey sludge was then distilled (behind a safety shield) under oil pump vacuum and using an oil bath that was taken up to 120° . Tris(methylseleno)borane (12.56 g, 77%) was obtained as a pale yellow liquid: b.p. $83-85^\circ$ (0.1 mm); NMR (CDCl_3) δ 2.17 (s). The material solidifies when stored at -10°C .

Preparation of 3,5-di-n-butyl-1,2,4,3,5-triselenodiborolane⁷² (36)

Selenium shot (13.4 g, 169.7 mmol) was placed in a round bottom flask (50 mL) equipped with a condenser, a rubber septum and a magnetic stir bar, under an atmosphere of argon. The exit needle was not removed during the experiment. Tributylborane (30.48 g, 167.3 mmol) was added to the reaction flask via syringe, and the flask placed in a 230° oil bath with magnetic stirring overnight. The total product was distilled through a

vigreux column (2 x 5 cm) collecting a bright yellow liquid (18.7 g, 89%), bp 117-125° (2.5 mm); m/e 375.9108 [calcd for $C_8H_{18}B_2^{80}Se_3$, 375.9090].

1-(Methylsulfinyl)-2-heptadecanone (25)

This compound was prepared from sodium hydride (1.8717 g, 44.5 mmol; 57% dispersion in oil) in DMSO (30 mL) and methyl palmitate (10.0 g, 37.0 mmol) in dry THF (10 mL) exactly according to the literature.²⁵ Work-up consisted of pouring the reaction mixture into water (300 mL), addition of HCl to pH 1 and extraction into $CHCl_3$ (400 mL). The $CHCl_3$ layer was washed three times with water (300 mL portions), dried (Na_2SO_4), filtered and evaporated. The residual paste was placed on a silica gel column (3 x 10 cm), eluted with $CHCl_3$ and then ether, the product coming in the ether fractions. The ether fractions were evaporated and the white solid residue recrystallized from ethyl acetate (30 mL) yielding 2.40 g (20%) white solid (m.p. 96.0-97.5°); IR ($CHCl_3$): 1708 cm^{-1} (C=O), 1030 cm^{-1} (S=O); NMR ($CDCl_3$) δ 1.7-0.8 (29H), 2.60 (t, J = 6 Hz, 2H), 2.68 (s, 3H), 3.77 (AB q, J = 14 Hz, 2H); m/e 315.2365 [calcd for $C_{18}H_{35}O_2S$ (M-1), 315.2358]. Anal. Calcd for $C_{18}H_{35}O_2S$: C, 68.30; H, 11.46; O, 10.11; S, 10.13. Found: C, 68.34; H, 11.39; S, 9.84.

(E)-1-(Phenylsulfinyl)-1-pentene (28)

This compound was prepared from bis(phenylsulfinyl)-methane¹³⁹ (4.79 g, 18.1 mmol), sodium hydride (0.7819 g, 18.2 mmol) and 1-bromobutane (2.94 g, 18.2 mmol) in dry HMPA (50 mL), followed by the addition of trimethyl phosphite (2.29 g, 18.5 mmol) after 12 h, exactly according to the literature.⁵ The work-up consisted of partitioning the reaction mixture between water (300 mL) and ether (500 mL), washing the ether layer with water (two times, 300 mL portions), drying (MgSO_4), filtration and evaporation. The residue was placed on an alumina column (2 x 60 cm) with gradient elution (5-10% ethyl acetate in hexane). Fractions containing product with R_f ca. 0.5 (alumina, 20% ethyl acetate in hexane) were evaporated and the residue distilled (Kugelrohr) yielding a pale yellow liquid (0.5957 g, 16.9%), b p 120° (0.20 mm); IR (neat) 1046 cm^{-1} ; NMR (CDCl_3) δ 0.90 (t, $J = 5$ Hz, 3H), 1.49 (hex., 2H), 2.09 (dt, 2H), 6.20 (d, $J = 15$ Hz, 1H), 6.60 (AXY dt, $J_{AX} = 6$ Hz, $J_{XY} = 15$ Hz, 1H), 7.2-7.8 (5H); m/e 194.0769 [calcd for $\text{C}_{11}\text{H}_{14}\text{OS}$, 194.0766].

Anal. Calcd. for $\text{C}_{11}\text{H}_{14}\text{OS}$: C, 68.00; H, 7.26; O, 8.23; S, 16.50. Found: C, 67.95; H, 7.32; S, 16.40.

1-(Phenylthio)-1-pentene (29)

This compound was prepared from dimethyl phenylsulfonmethanephosphonate^{140a} [eq. (48)] (11.50 g,

57.2 mmol), sodium hydride (2.42 g, 56.5 mmol, 56% dispersion in oil) and butanol (4.07 g, 56.4 mmol) in dry toluene (80 mL) according to the literature⁶⁹ procedure. After being stirred 2 h at 80°, the reaction mixture was washed with water (100 mL), dried (MgSO₄), the solvent evaporated and the residue distilled through a vigreux column (1 x 15 cm) to afford a colorless liquid (5.20 g, 51.7%), b.p. 103-106° (1.5 mm).^{140b} An IR spectrum (neat) was identical to a spectrum of the product isolated from the reduction of (28); NMR (CDCl₃) δ 0.8 (dt, 3H), 1.25-1.62 (m, 2H), 2.00-2.31 (m, 2H), 5.67-6.22 (m, 2H), 7.1-7.4 (5H).

Methyl phenoxymethylcephalosporin β -sulfoxide

Phenoxymethylcephalosporin β -sulfoxide (0.1044 g) was dissolved in CHCl₃ (20 mL), cooled to 0°, and ethereal diazomethane added dropwise with stirring until the yellow color persisted. The solvent was evaporated and the residue dissolved in a small amount of CHCl₃ and chromatographed on a silica gel column (2 x 15 cm) with ethyl acetate elution. Fractions containing material with R_f ca. 0.4 (silica gel, ethyl acetate) were evaporated yielding white needles (88.0 mg), mp 228-230° (dec.); IR (CHCl₃) 1800 (β -lactam), 1729, 1690, 1060 (S=O) cm⁻¹; m/e 378 (low resolution); NMR (CDCl₃) was consistent with published data.¹⁴²

Reduction of dibenzyl sulfoxide with (22) (entry 1a,
Table IV)

Tris(phenylseleno)borane (22) (0.8318 g, 1.736 mmol) was dissolved in dry CHCl_3 (2 mL) under a dry nitrogen atmosphere, and cooled to -30° . A solution of the sulfoxide (0.5129 g, 2.229 mmol) in dry CHCl_3 (1 mL) was added to the borane solution via syringe in one portion, and stirred 1.5 h at -30° . The reaction mixture was then filtered through an alumina column (1 x 7 cm) with CHCl_3 elution. The solvent was evaporated, and the yellow residue chromatographed on an alumina column (2 x 50 cm) with hexane elution. The solvent was removed from the fractions containing the sulfide, yielding a white crystalline solid (0.4383 g, 91.8%), mp $48-51^\circ$. The product had identical mp, IR, NMR, and R_f (alumina, hexane) to authentic dibenzyl sulfide.

Reduction of dibenzyl sulfoxide with (32) (entry 1b,
Table IV)

The sulfoxide (0.2844 g, 1.236 mmol) was dissolved in dry CHCl_3 (3 mL) and cooled to 0° under a dry nitrogen atmosphere. Tris(methylseleno)borane (32) (0.2782 g, 0.950 mmol) was added to the solution neat via syringe, and the solution stirred 0.25 h at 0° and 2.5 h at room temperature. The solvent was evaporated from the reaction

mixture, and the residue filtered through an alumina column (1 x 5 cm) with hexane elution until all sulfide had come off the column. The solvent was evaporated, and the yellow solid residue evacuated (<0.1 mm) overnight yielding white solid (0.2347 g, 88.7%), mp 48-50°.

The product had identical mp, IR, NMR, and R_f (alumina, hexane) to authentic dibenzyl sulfide.

Reduction of dibenzyl sulfoxide with (36) (entry 1c,
Table IV)

(a) The sulfoxide (0.1229 g, 0.534 mmol) was dissolved in dry CHCl_3 (3 mL) and the solution cooled to -30° under an inert atmosphere. Addition of neat 3,5-dibutyl-1,2,4,3,5-triselenodiborolane (36) (0.2120 g, 0.569 mmol) via syringe caused an immediate red precipitate. After 5 min at -30°, a further portion of borolane (0.0420 g, 0.113 mmol) was added, the solution stirred an additional 20 min at -30°, and the total product filtered through an alumina column (1 x 2 cm) with CHCl_3 elution. The solvent was evaporated, and the residue chromatographed on an alumina column (1 x 30 cm) with hexane elution. The fractions containing the sulfide were evaporated yielding a white crystalline solid (85.3 mg, 74.6%), mp 48-50°. The product had identical mp, IR, NMR, and R_f (alumina, hexane) to authentic dibenzyl sulfide.

(b) The sulfoxide (20.7 mg, 0.090 mmol) was

dissolved in dry CDCl_3 (0.5 mL) in an NMR tube and cooled to ca. -70° under a dry nitrogen atmosphere. The borolane (36) (98.2 mg, 0.264 mmol) was added to the tube resulting in a bright yellow solution. An NMR spectrum at a probe temperature of -55° showed a large singlet at δ 3.53, identical to dibenzyl sulfide. No other methylene signal was seen. Changing the probe temperature to -45° , -35° , and $+32^\circ$ resulted in no apparent change in the spectra. Above -35° , a red precipitate started to form.

Reduction of diphenylsulfoxide with (22) (entry 2, Table IV)

Tris(phenylseleno)borane (22) (1.2352 g, 2.579 mmol) was dissolved in dry CHCl_3 (1 mL) and cooled to 0° under a dry nitrogen atmosphere. The sulfoxide (0.7640 g, 3.778 mmol) was dissolved in dry CHCl_3 (1 mL) and added to the borane solution in one portion via syringe, followed by two 0.5 mL CHCl_3 rinses. The solution was stirred at 0° for 0.5 h, at room temperature for 1 h, and then filtered through an alumina column (1 x 5 cm) with CHCl_3 elution. The solvent was evaporated, and decane (0.6450 g) added to the yellow liquid as an internal standard. The residue was diluted with CHCl_3 (5 mL), and VPC¹⁴³ analysis, when compared to a VPC of a standard solution composed of authentic diphenyl sulfide (0.1753 g) and decane (0.1307 g) in CHCl_3 (1 mL), showed a yield of 91% sulfide. The solvent was evaporated from the

reaction mixture, the residue dissolved in methanol (10 mL) and NaBH_4 added in small portions until a faint yellow color was obtained. This mixture was immediately partitioned between 1 M NaOH (50 mL) and 30-60° petroleum ether (50 mL). The petroleum ether was dried (Na_2SO_4), filtered, evaporated, and the yellow residue chromatographed on an alumina column (1 x 20 cm) eluting with heptane. Colorless fractions containing the sulfide were evaporated and the product distilled in a Kugelrohr apparatus affording a colorless liquid, bp 180° (25 mm). The product had identical IR, NMR, R_f (alumina, hexane), and retention time (VPC) to authentic diphenyl sulfide.

Reduction of 2,2'-sulfinylbis(2-methylpropane) with (22)
(entry 3, Table IV)

Tris(phenylseleno)borane (22) (0.2902 g, 0.605 mmol) was dissolved in dry CHCl_3 (1 mL) and cooled to 0° under a nitrogen atmosphere. The sulfoxide (0.1322 g, 0.815 mmol) was dissolved in dry CHCl_3 (0.5 mL) and added to the borane solution in one portion via syringe, followed by a 0.5 mL CHCl_3 rinse. Dodecane (0.0898 g) was added to the solution, the cold bath removed, and the reaction followed by VPC.¹⁴⁴ Analysis of the solution by VPC after 1 h, when compared to a standard solution composed of di-t-butyl sulfide (0.1051 g) and dodecane (0.0838 g) in CHCl_3 (2 mL), showed a yield of 83.6%

sulfide. After 7 h at room temperature, the yield was 84.9%. Most of the solvent from the reaction mixture was evaporated, and the residue distilled (Kugelrohr apparatus) to afford a colorless liquid (CHCl_3 and sulfide by VPC), b p 120° (atmospheric pressure). This liquid was redistilled in the same manner, discarding an initial cut, and collecting a colorless liquid at 125° . The product had identical IR and retention time to authentic di-t-butyl sulfide.

Reduction of 1-(methylsulfinyl)-2-heptadecanone (25) with (22) (entry 5, Table IV)

Tris(phenylseleno)borane (22) (0.5875 g, 1.226 mmol) was dissolved in dry CHCl_3 (5 mL) and cooled to 0° under a dry nitrogen atmosphere. The ketosulfoxide (0.5823 g, 1.84 mmol) in dry CHCl_3 (3 mL) was added in one portion to the borane solution via syringe, followed by two 0.5 mL CHCl_3 rinses. After stirring 1 h at 0° and 1 h after removal of the cold bath, the solvent was evaporated and the residue chromatographed on an alumina column (2 x 20 cm) with 2% ethyl acetate in hexane. Fractions containing the product (26) were evaporated yielding a white solid (0.4555 g, 90.0%), mp $40-43^\circ$; IR (CCl_4) 1709 cm^{-1} ; NMR (CDCl_3) δ 0.8-1.7 (29H), 2.06 (s, 3H), 2.58 (t, $J = 7\text{ Hz}$, 2H), 3.15 (s, 2H); m/e 300.2489 [calcd for $\text{C}_{18}\text{H}_{36}\text{OS}$, 300.2487]. Anal. Calcd for $\text{C}_{18}\text{H}_{36}\text{OS}$: ✓

C, 71.93; H, 12.07; O, 5.32; S, 10.67. Found: C, 71.83; H, 11.89; S, 10.68.

Reduction of (E)-1-(phenylsulfinyl)-1-butene (28)

(entry 4, Table IV)

(a) Tris(phenylseleno)borane (22) (0.2067 g, 0.4315 mmol) was dissolved in dry CHCl_3 (3 mL) and cooled to 0° under a dry nitrogen atmosphere. The sulfoxide (0.1258 g, 0.647 mmol) in dry CHCl_3 (0.5 mL) was added in one portion via syringe to the borane solution, followed by two 0.5 mL CHCl_3 rinses. After stirring 0.5 h at 0° , the solvent was evaporated and the residue chromatographed on a silica gel column (1 x 40 cm) with hexane elution. Fractions containing the product (R_f ca. 0.5, silica gel, hexane) were evaporated, and the residue distilled (Kugelrohr) yielding a colorless liquid (0.0997 g, 86%), 110° at 25 mm.^{140b} NMR of this product was identical to that obtained from the Horner-Wittig reaction; IR (neat) 1585 cm^{-1} ; NMR (CDCl_3) δ 0.85 (dt, 3H), 1.30-1.65 (complex, 2H), 2.00-2.28 (complex, 2H), 5.70-6.23 (complex, 2H), 7.0-7.5 (5H); m/e 178.0820 [calcd for $\text{C}_{11}\text{H}_{14}\text{S}$, 178.0816].

(b) The sulfoxide (73.0 mg, 0.376 mmol) was dissolved in dry CDCl_3 (2 mL) and cooled to 0° under a

dry nitrogen atmosphere. Tris(methylseleno)borane (32) (103.5 mg, 0.353 mmol) was added neat via syringe. After 10 min. stirring at 0°, the solution was filtered (cotton wool) into an NMR tube. The spectrum was superimposable on that of the product isolated above, except for a large singlet at δ 2.53 due to dimethyl diselenide.

Analysis of vinyl sulfide products

1-(Phenylthio)-1-pentene (29) (0.4582 g, 2.570 mmol) from the Horner-Wittig reaction was dissolved in CH_2Cl_2 (30 mL) in a flask equipped with an addition funnel, and cooled to -30°. A solution of 85% *m*-chloroperoxybenzoic acid (0.5208 g, 2.51 mmol) in CH_2Cl_2 (10 mL) was added dropwise over a 10 min. period. After being stirred 0.5 h at -30°, the reaction mixture was washed with 5% NaHCO_3 (two 70 mL portions), washed once with water, dried (MgSO_4), filtered and evaporated. The residue was chromatographed on an alumina column (2.5 x 20 cm) and eluted initially with 5% ethyl acetate in heptane (100 mL), then 10% ethyl acetate in heptane, yielding two products. Fractions with the faster moving product (R_f ca. 0.5, alumina, 20% ethyl acetate in hexane) were evaporated yielding a colorless liquid (0.1880, 37.7%), judged to be (E)-1-(phenylsulfinyl)-1-pentene (28) on the basis that its proton NMR and IR spectra were identical to an authentic sample prepared above. Fractions

with the slower moving product (R_f ca. 0.45, alumina, 20% ethyl acetate in hexane) were evaporated yielding a colorless liquid (0.1865, 37.4%) judged to be (Z)-1-(phenylsulfinyl)-1-pentene (30) on the basis of the proton NMR data below: IR (neat): 1040 cm^{-1} ; NMR (CDCl_3) δ 1.00 (t, $J = 6\text{ Hz}$, 3H), 1.53 (hex., 2H, 2.4-2.8 (m, 2H), 6.20 (s, 2H; changed to ABq, $J = 9\text{ Hz}$ on addition of $\text{Eu}(\text{fod})_3$, irradi. δ 2.6), 7.40-7.70 (5H).

Reduction of methyl phenoxymethylcephalosporin β -sulf-oxide (31) with (36) (entry 7, Table IV)

The sulfoxide (106.6 mg, 0.282 mmol) was dissolved in dry CHCl_3 (10 mL) under a dry nitrogen atmosphere in a flask equipped with a reflux condensor. 3,5-Di-n-butyl-1,2,4,3,5-triselenodiborolane (36) (406.4 mg, 1.092 mmol) was added neat via syringe and the solution refluxed for 24 h. DMSO (64 mg) was added and the total reaction mixture chromatographed on a silica gel column (2.5 x 12 cm) with 4% ethyl acetate in CHCl_3 elution. The fractions containing the sulfide (R_f ca. 0.5, silica gel, 1:1 ethyl acetate, CHCl_3) were evaporated and chromatographed on a silica gel column (2.5 x 15 cm) with ether elution. Fractions containing the sulfide were evaporated and the pale yellow solid was recrystallized from ether (5 mL)-THF (2 drops) by cooling to ca. -70° . The white needles were collected, and recrystallized from ether

(6 mL)-THF (5 drops) by cooling to ca. -70° . The product was collected and washed with ca. -70° ether yielding white needles (29.2 mg, 28.6%), mp $128-130^{\circ}$. The literature¹⁴⁵ reports the sulfide mp $137-138^{\circ}$; however, IR and proton NMR data were identical to that reported in the literature.¹⁴⁵

Reduction of dibenzyl sulfoxide with (22) in the presence of an ester (entry 6, Table IV)

Tris(phenylseleno)borane (22) (0.4584 g, 0.958 mmol) was dissolved in dry CHCl_3 (1 mL) and placed under a dry nitrogen atmosphere. Methyl palmitate (0.7775 g, 2.874 mmol) was dissolved in dry CHCl_3 (1 mL) and added to the borane solution via syringe, along with two 0.5 mL CHCl_3 rinses. After stirring 12 h at room temperature, the sulfoxide (0.3128 g, 1.360 mmol) in dry CHCl_3 (1 mL) was added to the solution via syringe, along with two 0.5 mL CHCl_3 rinses. After stirring 1 h at room temperature, the solvent was evaporated and the residue chromatographed on a silica gel column (2 x 24 cm) with hexane elution. The colorless fractions containing the sulfide and ester (R_f ca. 0.5 and 0.3, respectively, alumina, hexane) were evaporated and chromatographed on an alumina column (2 x 50 cm) with hexane elution. The fractions containing the sulfide were evaporated yielding a white crystalline solid (0.2461 g, 84.6%), mp $47-49^{\circ}$. The product had

identical mp, IR, NMR, and Rf as authentic dibenzyl sulfide. The fractions containing the ester were evaporated yielding a white waxy solid (0.5613 g, 78.2%), mp 28-31°. The product had mp, IR, NMR, and Rf identical with authentic methyl palmitate.

Preparation of Selenoacetals¹⁴⁶

3,3-Bis(phenylseleno)-5 α -cholestane (entry 1, Table V)

(a) Without acid catalysis. A solution of 5 α -cholestan-3-one (160 mg, 0.42 mmol) in dry CH₂Cl₂ (1 mL) was injected over 10 min. to a stirred solution of tris(phenylseleno)borane (22) (131 mg; 0.27 mmol) in CH₂Cl₂ (2 mL) that was cooled by a bath set at -30°C. More CH₂Cl₂ (2 x 5 mL) was used to rinse all the ketone from its initial containing-flask into the reaction vessel. After 30 min. considerable ketone was still present (TLC). The reaction vessel was allowed to warm to room temperature (over about 1 h) and left for a further 1 h, by which time no starting ketone remained (TLC). The solvent was evaporated and chromatography of the residue over alumina (2 x 20 cm) with pentane afforded 252 mg (89%) of selenoacetal as a homogeneous (TLC, alumina, pentane) oil; NMR (CDCl₃) δ 0.2-2.2 (m, incorporating br s at 0.35 and 0.56, 46H), 7-7.9 (m, 10H). The material was identical with a sample made⁸² by

treating an ethereal mixture of 5 α -cholestanone and benzeneselenol with HCl gas. The latter sample had exact mass 526.3069 [calcd. for C₃₃H₅₀⁸⁰Se (M-PhSe), 526.3078] and was analyzed. Anal. Calcd for C₃₉H₅₆Se₂: C, 68.60; H, 8.27. Found: C, 68.67; H, 8.27.

(b) With acid catalysis. A solution of 5 α -cholestan-3-one (98 mg, 0.25 mmol) in CHCl₃ (0.5 mL) was injected with stirring into a flask containing tris-(phenylseleno)borane (22) (82 mg, 0.17 mmol). More CHCl₃ (2 x 0.5 mL) was used to rinse the ketone from its initial containing-flask into the reaction vessel. TFA (2 μ L, 0.026 mmol) was added to the reaction mixture. No ketone remained after 40 min (TLC). The solution was placed on a column (1 x 3 cm) of alumina. Elution with CHCl₃ (50 mL) gave a crude product which was purified by PLC (one alumina plate developed with pentane). The appropriate band was eluted with CHCl₃ to afford 152 mg (88%) of selenoacetal as a homogeneous (TLC, alumina, pentane) oil identical with an authentic specimen.⁸²

2,2-Bis(phenylseleno)tricyclo[3.3.1.1^{3,7}]decane (entry 2,
Table V)

(a) Without acid catalysis. Tricyclo[3.3.1.1^{3,7}]-decan-2-one (66 mg, 0.44 mmol) in CHCl₃ (0.5 mL) was injected with stirring into a flask containing tris-

(phenylseleno)borane (22) (149 mg, 0.311 mmol). More CHCl_3 (2 x 0.5 mL) was used to rinse the contents of the syringe into the reaction vessel. After a reaction period of 24 h the mixture was applied to a column of alumina (1.5 x 3 cm) made up with CHCl_3 . More CHCl_3 (150 mL) was passed through the column and the eluate was evaporated. The product was separated by PLC (one alumina plate developed with pentane). The appropriate band was eluted with CHCl_3 and the solution was evaporated to give 165 mg (84%) of selenoacetal as a homogeneous (TLC, alumina, pentane), colorless solid: mp 152-155°C; NMR (CDCl_3) δ 1.44-2.20 (m, 10H), 2.6-3.0 (m, 4H), 7.12-7.45 (m, 6H), 7.62-7.9 (m, 4H). Analytically pure material from a different experiment⁸² had mp 153-154°C; exact mass 291.0648 [calcd. for $\text{C}_{16}\text{H}_{19}^{80}\text{Se}$ (M-PhSe), 291.0652]. Anal. Calcd for $\text{C}_{22}\text{H}_{24}\text{Se}_2$: C, 59.20; H, 5.42. Found: C, 59.32; H, 5.44.

(b) With acid catalysis. Tricyclo[3.3.1.1^{3,7}]-decan-2-one (45.4 mg, 0.302 mmol) in CHCl_3 (0.5 mL) was injected with stirring into a flask containing tris-(phenylseleno)borane (22) (96.5 mg, 0.202 mmol). More CHCl_3 (2 x 0.5 mL) was used to rinse the contents of the syringe into the reaction vessel. TFA (2 μL , 0.026 mmol) was injected immediately. After 1 h the reaction mixture was applied to a column of alumina (1 x 3 cm)

made up with CHCl_3 . More CHCl_3 (50 mL) was passed through the column and the eluate was evaporated. The product was separated by PLC (one alumina plate developed with pentane). The appropriate band was eluted with CHCl_3 and the solution was evaporated to give 85.5 mg (63%) of selenoacetal; mp 152-155°C.

5,5-Bis(phenylseleno)nonane (entry 3, Table V)

(a) Use of *p*-toluene sulfonic acid. Nonan-5-one (98 mg, 0.69 mmol) and then one crystal of *p*-toluene sulfonic acid monohydrate were added to a stirred solution of tris(phenylseleno)borane (22) (231 mg, 0.48 mmol) in CHCl_3 (3 mL). Some ketone appeared to be present (TLC) after 2 h. After an overnight reaction period the solvent was evaporated and the product was separated by PLC (one alumina plate developed with pentane). The appropriate band was eluted with CHCl_3 . Evaporation afforded 242 mg (80%) of selenoacetal as a homogeneous (TLC, alumina, pentane) oil, identical to a sample made using TFA.

(b) Use of TFA. Nonan-5-one (35 mg, 0.24 mmol) and then TFA (2 μL , 0.026 mmol) were injected into a stirred solution of tris(phenylseleno)borane (22) (76 mg, 0.16 mmol) in CHCl_3 (2 mL). After an arbitrary period of 1 h the mixture was applied to a column of

alumina (1 x 3 cm) made up with CHCl_3 . More CHCl_3 (60 mL) was passed through the column and the eluate was evaporated. The product was separated by PLC (one alumina plate developed with pentane). The appropriate band was eluted with CHCl_3 . Evaporation of the solvent gave 79 mg (73%) of the selenoacetal as a colorless, analytically pure oil.¹⁴⁷ Anal. Calcd for $\text{C}_{21}\text{H}_{28}\text{Se}_2$: C, 57.54; H, 6.44. Found: C, 57.50; H, 6.49.

1,1-Bis(phenylseleno)undecane²³ (entry 4, Table V)

(a) Use of *p*-toluene sulfonic acid. Undecanal (114 mg, 0.67 mmol) and then *p*-toluenesulfonic acid monohydrate (ca. 0.1 mg) were added to a stirred solution of tris(phenylseleno)borane (22) (222 mg, 0.46 mmol) in CHCl_3 (3 mL). After an arbitrary period of 4 h the solvent was evaporated and the product was separated by PLC (one alumina plate developed with pentane). The appropriate band was eluted with CHCl_3 and the solution was evaporated to yield 243 mg (78%) of the selenoacetal as a homogeneous (TLC, alumina, pentane) oil:¹⁴⁸ NMR (CDCl_3) δ 0.7-2.12 (m, 21H), 4.45 (t, 1H, $J = 6.4$ Hz), 7.1-7.34 (m, 6H), 7.38-7.66 (m, 4H); m/e 468.0382 [calcd for $\text{C}_{23}\text{H}_{32}^{80}\text{Se}_2$, 468.0834].

(b) Use of TFA. Undecanal (62 mg, 0.364 mmol) and then TFA (2 μL , 0.026 mmol) were injected into a

stirred solution of tris(phenylseleno)borane (22) (122 mg, 0.25 mmol) and CHCl_3 (2 mL). After an arbitrary period of 1 h the mixture was applied to a column (1 x 3 cm) of alumina made up with CHCl_3 . More CHCl_3 (50 mL) was passed through the column and the eluate was evaporated. The product was separated by PLC (one alumina plate developed with pentane). The appropriate band was eluted with CHCl_3 and the solution was evaporated to afford 135 mg (79%) of the selenoacetal as a colorless oil identical with material made using *p*-toluenesulfonic acid.

4-t-Butyl-1,1-bis(phenylseleno)cyclohexane (entry 5, Table V)

4-t-Butyl-cyclohexanone (292 mg, 1.90 mmol) in CHCl_3 (1 mL) was injected into a stirred solution of tris(phenylseleno)borane (22) (618 mg, 1.29 mmol) in CHCl_3 (2 mL). Three portions (0.5 mL each) of CHCl_3 were used to rinse the contents of the syringe into the reaction vessel. TFA (5 μL , 0.65 mmol) was then added to the mixture. After 18 h the solvent was evaporated and the residue was dissolved in a mixture of methanol (3 mL) and benzene (3 mL). NaBH_4 was added in small portions to the stirred solution until only a very pale yellow color persisted. The mixture was immediately partitioned between pentane (100 mL) and 5% w/v aqueous Na_2CO_3 (50 mL). The organic layer was washed once with water, dried and evaporated. Chromatography of the residue over

alumina (3 x 50 cm) with pentane and removal of the solvent gave 686 mg (80%) of the selenoacetal as a pale yellow, homogeneous (TLC, alumina, pentane) and analytically pure (despite 8° melting range) solid: mp 81-89°C; NMR (CDCl₃) δ 0.6-2.25 (m, incorporating a singlet at 0.8, 18H), 7.1-7.95 (m, 10H); m/e 452.0543 [calcd for C₂₂H₂₈⁸⁰Se₂, 452.0521]. Anal. Calcd for C₂₂H₂₈Se₂: C, 58.67; H, 6.27. Found: C, 58.66; H, 6.30. Crystallization from 2:1 methanol-acetone gave plates: mp 89-91°.

1,1-Bis(phenylseleno)cyclopentane (entry 6, Table V)

Cyclopentanone (145 mg, 1.73 mmol) was injected into a stirred solution of tris(phenylseleno)borane (22) (583 mg, 1.22 mmol) in CHCl₃ (3 mL). TFA (5 μ L, 0.065 mmol) was added. After 3 h¹⁴⁹ the solvent was evaporated and the residue was dissolved in MeOH (3 mL). NaBH₄ was added in small portions to the stirred solution until the yellow color was discharged. The mixture was immediately partitioned between pentane (50 mL) and 5% w/v aqueous Na₂CO₃ (50 mL). The pentane layer was washed once with water, dried and evaporated. Chromatography of the residue over alumina (3 x 5 cm) with pentane gave 319 mg (48%) of the selenoacetal as a white, homogeneous (TLC, alumina, pentane) solid; NMR (CDCl₃) δ 1.4-2.2 (m, 8H), 7.1-7.5 (m, 6H), 7.5-7.9 (m, 4H); m/e

225.0153 [calcd for $C_{11}H_{13}^{80}Se$ (M-PhSe) 225.0182]. No further purification was needed for analysis. Anal. Calcd for $C_{17}H_{18}Se_2$: C, 53.70; H, 4.77. Found: C, 53.90, H, 4.85. Crystallization from 2:1 methanol-acetone gave plates: mp 73-75°C.

[1,1-Bis(phenylseleno)ethyl]benzene (entry 7, Table V)

Acetophenone (35 mg, 0.29 mmol), and then TFA (2 μ L, 0.026 mmol) were injected into a stirred solution of tris(phenylseleno)borane (22) (104 mg, 0.22 mmol) and $CHCl_3$ (2 mL). After an arbitrary period^{150a} of 1 h the mixture was applied to a column (1 x 3 cm) of alumina made up with $CHCl_3$. More $CHCl_3$ (50 mL) was passed through the column and the eluate was evaporated. The product was separated by PLC (one alumina plate developed with pentane). The appropriate band was eluted with $CHCl_3$ and the solution was evaporated to afford 63 mg (52%) of the selenoacetal as a colorless analytically pure oil.^{150b} Anal. Calcd for $C_{20}H_{18}Se_2$: C, 57.71; H, 4.36. Found: C, 57.72; H, 4.54.

1-(2-Naphthyl)-1,1-bis(phenylseleno)ethane (entry 8, Table V)

2-Acetylnaphthalene (104 mg, 0.61 mmol) in $CHCl_3$ (0.5 mL) was injected into a stirred solution of tris-

(phenylseleno)borane (22) (202 mg, 0.42 mmol) in CHCl_3 (1.5 mL). More CHCl_3 (2 x 0.5 mL) was used to rinse all the ketone from its initial container into the reaction vessel. TFA (1 μL , 0.013 mmol) was added to the mixture resulting in the formation of a deep red color. After 3.5 h a trace of ketone remained.^{151a} The solvent was evaporated and the selenoacetal was isolated as a yellow oil (98.5 mg, 34%) by chromatography over alumina (1 x 50 cm) with 99:1 hexane-ethyl acetate. Crystallization from hexane (1 mL) gave 82 mg (28%) of the selenoacetal as a solid: mp 86-91°. Pure material^{151b} has mp 88-92°.

1,1-Bis(phenylseleno)undecane (entry 1, Table VI)

A magnetically stirred mixture of tris(phenylseleno)borane (22) (368 mg, 0.77 mmol) in CHCl_3 (4 mL) was cooled in an ice bath. 1,1-Dimethoxyundecane¹⁵² (55) (228 mg, 1.05 mmol) was added from a syringe over 4 min and then TFA (15 μL , 0.20 mmol) was injected in one portion. After 0.5 h the ice bath was removed and the stirring was continued for 1 h. The solvent was evaporated and the residue, in a little CHCl_3 , was applied to two alumina PLC plates which were developed with hexane. The appropriate bands were extracted with ethyl acetate. Evaporation of the solvent gave 422 mg (85%) of the selenoacetal as a homogeneous (TLC alumina/hexane), colorless oil:¹⁴⁸

NMR (CDCl_3) δ 0.7-2.1 (m, 21H), 4.45 (t, 1H, $J = 6.4$ Hz) 7.2 (m, 6H), 7.55 (M, 4H); m/e 468.0834 [calcd for $\text{C}_{23}\text{H}_{32}^{80}\text{Se}_2$, 468.0834].

5,5-Bis(phenylseleno)nonane (entry 2, Table VI)

The reaction and isolation were carried out as described above using tris(phenylseleno)borane (22) (381 mg, 0.80 mmol), dry CHCl_3 (3 mL), acetal¹⁵³ (221 mg, 1.17 mmol), and TFA (15 μL , 0.20 mmol). The product was obtained as a colorless, homogeneous (TLC, alumina, hexane) oil¹⁴⁷ which weighed 427 mg (83%): NMR (CDCl_3) δ 0.8 (t, $J = 6.6$ Hz), 1.15 (m), 1.62 (m; signals at 0.8-1.62 correspond to 18H), 7.25 (m, 6H), 7.67 (m, 4H); m/e 440.0530 [calcd for $\text{C}_{21}\text{H}_{28}^{80}\text{Se}_2$, 440.0521].

1,1-Bis(phenylseleno)ethylbenzene (entry 3, Table VI)

The acetal¹⁵⁴ (145 mg, 0.87 mmol) was added from a syringe over ca. 5 min to a magnetically stirred mixture of tris(phenylseleno)borane (22) (320 mg, 0.67 mmol) and CHCl_3 (5 mL). TFA (6 μL , 0.08 mmol) was added, the mixture was stirred for 3 h and then the solvent was evaporated. The residue was stirred (open to the atmosphere) for 2 h with THF (3 mL) and water (2 drops). The solvent was evaporated and residue was chromatographed on an alumina column (1.5 x 30 cm) with hexane to afford

291 mg (80%) of the selenoacetal as a pure (TLC, alumina-hexane), colorless oil: ^{150}b NMR (CDCl_3) δ 2.03 (s, 3H), 6.9-7.63 (m, 15H); m/e 417.9733 [calcd for $\text{C}_{20}\text{H}_{18}^{80}\text{Se}_2$, 417.9739].

1-(2-Naphthyl)-1,1-bis(phenylseleno)ethane (entry 4,
Table VI)

A magnetically stirred mixture of tris(phenylseleno)borane (22) (719 mg, 1.50 mmol) in dry CH_2Cl_2 (2 mL) was cooled in a bath kept at -30°C . The acetal¹⁵⁵ (482 mg, 2.25 mmol) in CH_2Cl_2 (1 mL) was added over 7 min from a syringe. [More CH_2Cl_2 (2 x 0.5 mL) was used to rinse the remaining contents of the syringe into the reaction vessel.] TFA (15 μL , 0.02 mmol) was added and, after 30 min, the cooling bath was removed. Stirring was continued for 1.5 h more and the reaction mixture was placed onto the top of a column of alumina (1 x 5 cm) made up with CH_2Cl_2 . Elution with CH_2Cl_2 (100 mL) and evaporation gave a residue which was dissolved in boiling hexane (17 mL). The solution was allowed to cool to room temperature and was then stored at 5°C for 1 h. The resulting crystals were washed with a little cold (-10°C) hexane. A second crop was obtained by cooling the combined filtrate and washings to -10°C . The total solids were recrystallized in the same way from hexane (7 mL) to

give 663 mg of the selenoacetal as pale yellow crystals. The filtrates from the crystallizations were evaporated and a further 90 mg of product was obtained by PLC (one alumina plate developed with 1:20 ethyl acetate-hexane) followed by crystallization from hexane (2 mL). Total yield of homogeneous (TLC, alumina, 1:2 ethyl acetate-hexane) product; ¹⁵¹b 753 mg (71%); mp 88-92°; NMR (CDCl₃) δ 2.14 (s, 3H), 6.98-8.1 (m, 17H); m/e 311.0326 [calcd for C₁₈H₁₅⁸⁰Se (M-PhSe), 311.0339]. Anal. Calcd for C₂₄H₂₀Se₂: C, 61.81; H, 4.32. Found: C, 61.86; H, 4.56.

1-[Bis(phenylseleno)methyl]naphthalene (entry 5, Table VI)

With the differences noted below, this reaction was carried out as described for entry 3, Table VI using tris(phenylseleno)borane (22) (1.038 g, 2.17 mmol), CHCl₃ (5 mL), acetal¹⁵⁶ (648 mg, 3.20 mmol), and TFA (8 μL, 0.10 mmol). After a 3 h reaction period the solvent was evaporated and the product was isolated from the residue by PLC using three silica plates which were developed with 1:40 ethyl acetate-hexane. The appropriate bands were extracted with ethyl acetate and the solution was evaporated to afford 1.299 g (89%) of selenoacetal as a pure (TLC, alumina, 5:95 ethyl acetate-hexane), pale yellow oil; NMR (CDCl₃) δ 6.12 (br, 1H),

6.85-7.84 (m, 16H), 8.09 (br, 1H); m/e 453.9728 [calcd for $C_{23}H_{18}^{80}Se_2$ 453.9738]. Anal. calcd for $C_{24}H_{20}Se$: C, 61.07; H, 4.01. Found: C, 61.06; H, 4.02. At 60°C the broad NMR signal originally at δ 6.12 is sharper ($W_{1/2}$ 4 Hz) and is now at δ 6.21.

Tris(phenylseleno)methane⁷⁵ (entry 6, Table VI)

Neat 1,1,1-triethoxymethane (0.3539 g, 2.39 mmol) was injected via syringe into a solution of tris(phenylseleno)borane (22) (1.1466 g, 2.39 mmol) in dry $CHCl_3$ (5 mL), followed by TFA (5 μ L, 0.65 mmol). After stirring overnight at room temperature, the solvent was evaporated and the yellow solid residue was recrystallized from hexane (10 mL) (cool to -10°) yielding tan crystals (0.8422 g) mp 89-95°. The mother liquor was evaporated and the residue recrystallized from hexane (0.5 mL) (cooled to -10°) yielding tan crystals (32.2 mg), mp 90-95°, for a total yield of 87.4 mg (76.1%); NMR ($CDCl_3$) δ 7.5 (m, 6H), 7.2 (m, 9H), 5.40 (s, 1H).

1,1,1-Tris(phenylseleno)ethane⁷⁵ (entry 7, Table VI)

Neat 1,1,1-trimethoxyethane (145.0 mg, 1.21 mmol) was injected via syringe into a solution of tris(phenylseleno)borane (22) (690.1 mg, 1.44 mmol) in dry $CHCl_3$ (5 mL), followed by TFA (15 μ L, 0.195 mmol). After 1 h

stirring, TLC (alumina, hexane) showed methyl phenyl selenide¹⁵⁷ (R_f ca. 0.6) and another product (R_f ca. 0.2). After 2 h, TFA (20 μ L, 0.26 mmol) was added, followed by another TFA (100 μ L, 1.30 mmol) injection after another 2 h. The solution was stirred an additional 1.5 h, the solvent evaporated, and the residue recrystallized twice from cyclohexane (3 mL each time) yielding white crystals (152.2 mg, 25.5%), mp 145-155°; NMR (CDCl_3) δ 7.8 and 7.4 (m, 15H), 1.82 (s, 3H).

5,5-Bis(methylseleno)nonane (entry 1, Table VII)

Tris(methylseleno)borane (32) (207 mg, 0.71 mmol) and then TFA (6 μ L, 0.077 mmol) were injected into a stirred solution of nonan-5-one (142 mg, 1.00 mmol) in CHCl_3 (3 mL). The mixture became warm and a faint yellow color developed. After 15 min the reaction appeared to be complete (TLC control) but, as the starting ketone does not show up well on TLC plates, the mixture was arbitrarily left for a further 30 min. It was then evaporated and the residue was placed onto a small column (1 x 2 cm) of alumina made up with hexane. The appropriate fractions (TLC, alumina, heptane) were combined and evaporated. The resulting oil was distilled in a Kugelrohr to afford 285 mg (90%) of analytically pure selenoacetal as a colorless liquid: bp 80°C (0.1 mm); NMR (CDCl_3) δ 1.8-2.1 (m, incorporating sharp singlet at 1.95);

m/e 316.0220 [calcd for $C_{11}H_{24}^{80}Se_2$, 316.0209]. Anal.
 Calcd for $C_{11}H_{24}Se_2$: C, 42.04, H, 7.70. Found: C, 42.17;
 H, 7.93.

1,1-Bis(methylseleno)undecane (entry 2, Table VII)

Tris(methylseleno)borane (32) (180 mg, 0.61 mmol) and then TFA (5 μ L, 0.065 mmol) were injected into a stirred solution of undecanal (150 mg, 0.88 mmol) in $CHCl_3$ (5 mL). After 28 h at room temperature a further portion (40 μ L, 0.519 mmol) of TFA was added. After a further 3 h the composition of the mixture appeared to be static (TLC). The solvent was removed and the residue was dissolved in MeOH (2 mL). $NaBH_4$ was added in small portions to the stirred solution until the yellow color was discharged. The mixture was immediately partitioned between pentane (60 mL) and 5% w/v aqueous Na_2CO_3 (50 mL). The pentane layer was dried (Na_2SO_4) and evaporated. Kugelrohr distillation gave 201 mg (66%) of the selenoacetal as a pale yellow, homogeneous (TLC, alumina, hexane) liquid: bp 108°C (0.025 mm); NMR ($CDCl_3$) δ 0.7-2.2 (m, incorporating s at 2.0, 27H), 3.9 (t, J = 7 Hz, 1H); m/e 344.0532 [calcd for $C_{13}H_{28}^{80}Se_2$, 344.0522]. Anal. Calcd for $C_{13}H_{28}Se_2$: C, 45.62, H, 8.24. Found: C, 45.78; H, 8.32. When the above experiment was repeated in an NMR tube but with the initial relative proportion of TFA increased 8.3 fold [i.e., TFA (10 μ L with undecanal

(0.212 mmol) in CDCl_3 (ca. 0.5 mL, containing tris(methylseleno)borane (0.144 mmol)] the reaction appeared to be complete within 2.5 h.

4-t-Butyl-1,1-bis(methylseleno)cyclohexane (entry 4,

Table VII)

4-t-Butyl-cyclohexanone (233 mg, 1.51 mmol) in CHCl_3 (1 mL) was injected with stirring into a flask containing tris(methylseleno)borane (32) (310 mg, 1.06 mmol). Two portions (0.5 mL each) of CHCl_3 were used to rinse the contents of the syringe into the reaction vessel. TFA (5 μL , 0.065 mmol) was added to the mixture. A precipitate formed immediately. After an arbitrary period of 50 min the solvent was evaporated and the residue was dissolved in MeOH (2 mL). NaBH_4 was added in small portions to the stirred solution until the yellow color was discharged. The mixture was immediately partitioned between pentane (70 mL) and 5% w/v aqueous Na_2CO_3 (50 mL). The pentane layer was washed once with water, dried (Na_2SO_4) and evaporated. Kugelrohr distillation gave 446 mg (90%) of the selenoacetal as a colorless, homogeneous (TLC, alumina, pentane) liquid: bp 95°C (0.025 mm); NMR (CDCl_3) δ 0.86 (s, 9H); 1.5-2.2 (m, incorporating two singlets at 1.90 and 1.97, 15H); m/e 328.0211 [calcd for $\text{C}_{12}\text{H}_{24}^{80}\text{Se}_2$, 328.0209]. Anal. Calcd for $\text{C}_{12}\text{H}_{24}\text{Se}_2$: C, 44.18; H, 7.42. Found: C, 44.02; H, 7.42.

1,1-Bis(methylseleno)cyclopentane (entry 3, Table VII)

Cyclopentanone (138 mg, 1.64 mmol) was injected into a stirred solution of tris(methylseleno)borane (32) (352 mg, 1.20 mmol) in CHCl_3 (2 mL). TFA (5 μL , 0.065 mmol) was added and an immediate precipitate formed on the walls of the reaction flask. After an arbitrary period of 20 min the solvent was evaporated and the residue was diluted with MeOH (2 mL). NaBH_4 was added in small portions to the stirred solution until the yellow color was discharged. The mixture was immediately partitioned between pentane (50 mL) and 5% w/v aqueous Na_2CO_3 (50 mL). The pentane layer was washed once with water, dried (Na_2SO_4) and evaporated. Kugelrohr distillation gave 405 mg (96%) of the selenoacetal as a colorless, homogeneous (TLC, alumina, hexane) liquid: bp 93° (0.6 mm); NMR (CDCl_3) δ 1.6-2.2 (m, incorporating singlet at 1.99); m/e 257.9437 [calcd for $\text{C}_7\text{H}_{14}^{80}\text{Se}_2$, 257.9426]. Anal. Calcd for $\text{C}_7\text{H}_{14}\text{Se}_2$: C, 32.83; H, 5.51. Found: C, 32.93; H, 5.51.

1-(2-Naphthyl)-1,1-bis(methylseleno)ethane (entry 5, Table VII)

Tris(methylseleno)borane (32) (259 mg, 0.88 mmol) and then TFA (4 μL , 0.052 mmol) were injected into a stirred solution of 2-acetylnaphthalene (214 mg, 1.27

mmol) in CHCl_3 (5 mL). After 1 h only a trace of the ketone remained (TLC) and, after a further 1 h, the mixture was partitioned between CHCl_3 (30 mL) and water (30 mL). The organic layer was dried (Na_2SO_4) and evaporated. Chromatography of the residue over alumina (3 x 60 cm) with 49:1 hexane-ethyl acetate gave 369 mg (85%) of the selenoacetal as a pale yellow, homogeneous (TLC, alumina, 95:5 hexane-ethyl acetate) oil: NMR (CDCl_3) δ 1.9 (s, 6H), 2.39 (s, 3H), 7.35-8.60 (m, 2H), 7.6-8.05 (m, 5H); m/e 249.0163 [calcd for $\text{C}_{13}\text{H}_{13}^{80}\text{Se}$ (M-MeSe), 249.0182]. Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{Se}_2$: C, 49.14; H, 4.71. Found: C, 49.05; H, 4.58.

1-[Bis(methylseleno)methyl]naphthalene (entry 6, Table VII)

Tris(methylseleno)borane (32) (236 mg, 0.81 mmol) was injected into a stirred solution of 1-naphthaldehyde (176 mg, 1.13 mmol) in CHCl_3 (5 mL). Heat was generated but the solution remained clear. TFA (4 μL , 0.052 mmol) was added 5 min after mixing and a bulky precipitate formed immediately. After an arbitrary additional period of 30 min the mixture was partitioned between CHCl_3 (60 mL) and water (50 mL). The organic layer was dried (Na_2SO_4) and evaporated. Chromatography of the residue over alumina (3 x 10 cm) with 1:99 benzene-hexane gave 343 mg (92%) of the selenoacetal as a colorless and

homogeneous (TLC, alumina, 5:95 benzene-hexane) liquid;
 NMR (CDCl_3) δ 1.97 (s, 6H), 5.8 (br s, 1H), 7.2-7.95
 (m, 7H); m/e 329.9435 [calcd for $\text{C}_{13}\text{H}_{14}^{80}\text{Se}_2$,
 329.9426]. Anal. Calcd for $\text{C}_{13}\text{H}_{14}\text{Se}_2$: C, 47.58; H, 4.30.
 Found: C, 47.50; H, 4.33.

3- β -Acetoxy-20,20-bis(methylseleno)pregn-5-ene (entry 7,
Table VII)

Tris(methylseleno)borane (32) (294 mg, 1.01 mmol)
 and then TFA (20 μL , 0.26 mmol) were injected into a
 stirred solution of 3 β -acetoxy-20,20-bis(methylseleno)pregn-5-ene-20-one¹⁵⁸
 (513 mg, 1.43 mmol) in CHCl_3 (5 mL). After 26 h at room
 temperature only a trace of starting ketone was detectable
 by TLC (silica, CHCl_3). The mixture was partitioned
 between CHCl_3 (20 mL) and water (10 mL) and the organic
 phase was dried and evaporated. The residue was purified
 by chromatography over silica gel (3 x 30 cm; elution
 with CHCl_3). Appropriate fractions were combined and
 evaporated to afford 655 mg of the selenoacetal. Re-
 crystallization from a mixture of acetone (1 mL) and MeOH
 (5 mL) gave 607 mg (79%) of the product as a white homo-
 geneous (TLC, silica, CHCl_3) solid: mp 153-156°. A
 portion (85.3 mg) was recrystallized from EtOAc (1.5 mL)
 to give 62.4 mg of the selenoacetal with mp 159-161°C.
 This sample had IR (CHCl_3) 1722 cm^{-1} ; NMR (CDCl_3) δ
 0.7-2.7 (m, 38H), 4.35-4.80 (m, 1H), 5.25-5.45 (m, 1H);

m/e 437.1972 [calcd for $C_{24}H_{37}O_2^{80}Se$ (M-MeSe), 437.1958]. Satisfactory analytical data could not be obtained for this compound. Supporting evidence for the structure comes from the properties of the product obtained (73%) by Ph_3SnH -reduction;⁸² mp 148-149; $[\alpha]_D^{25}$ -61.16° (c 0.5, $CHCl_3$). 3 β -Acetoxypregn-5-ene has mp 147-148; $[\alpha]_D^{25}$ -62° (c 3.66, $CHCl_3$).¹⁵⁹

3-Methoxy-17,17-bis(methylseleno)estra-1,3,5(10)-triene
(entry 8, Table VII)

Tris(methylseleno)borane (32) (239 mg, 0.832 mmol) and then TFA (5 μ L, 0.068 mmol) were injected into a stirred solution of estrone methyl ether¹⁶⁰ (345 mg, 1.21 mmol) in $CHCl_3$ (4 mL). After 3.5 h only a trace of the starting ketone was detectable by TLC (silica, $CHCl_3$). The mixture was partitioned between water (50 mL) and $CHCl_3$ (50 mL). The organic layer was dried (Na_2SO_4) and evaporated. The residue was dissolved in hot acetone (8 mL) and the solution was cooled to afford crystals (batch A). More of the desired product was isolated from the mother liquors by chromatography over silica (2 x 40 cm) with 1:1 benzene-hexane. Batch A was recrystallized from acetone (10 mL) to afford 127.1 mg (batch B) of the selenoacetal (mp 134-135°C). The material from the chromatography was recrystallized from the mother liquors from batch B. A further crop (65.9 mg; mp 133-135°C;

batch C) of the product was obtained and the mother liquors from this batch C gave a final portion (127.7 mg; mp 133-135°) of the product when concentrated and crystallized from acetone (1.5 mL). The total yield of selenoacetal amounted to 320.7 mg (58%). Material from another, similar experiment was analyzed after crystallization from acetone and had NMR (CDCl_3) δ : 0.85-2.95 [m, incorporating a singlet at 1.02, and two partially resolved singlets at 2.02, 24H], 3.72 (s, 3H), 6.5-6.8 and 7.05-7.28 (m, 3H); m/e 362.1148 [calcd for $\text{C}_{20}\text{H}_{26}\text{OSe}$ (M-MeSeH), 362.1149]. Anal. Calcd for $\text{C}_{21}\text{H}_{30}\text{OSe}_2$: C, 55.26; H, 6.63; O, 3.51. Found: C, 55.51; H, 6.75; O, 3.80.

3,3-Bis(methylseleno)cholest-4-ene (entry 9, Table VII)

Tris(methylseleno)borane (32) (498 mg, 1.70 mmol) and then TFA (10 μL , 0.130 mmol) were injected into a stirred, ice-cold solution of cholest-4-en-3-one¹⁶¹ (942 mg, 2.45 mmol) in CHCl_3 (20 mL). After 1.5 h the pale yellow solution contained a considerable amount of starting ketone (TLC). The ice bath was removed and TFA (40 μL , 0.519 mmol) was added. After a further 17.5 h very little starting material remained (TLC). The mixture was shaken with water (10 mL), dried (Na_2SO_4) and evaporated. Chromatography of the residue over silica gel (3 x 50 cm) with hexane gave 433 mg (31%) of the

selenoacetal as a colorless, homogeneous (TLC, alumina, hexane) but unstable oil that crystallized slowly at -10°C ; NMR (CDCl_3) δ 5.49 (br. s, $w_{1/2}$ 4 Hz, 1H), 0.6-2.45 (m, incorporating singlets at 2.00 and 2.09, 49H); m/e 462.2777 [calcd for $\text{C}_{28}\text{H}_{46}^{80}\text{Se}$ (M- CH_2Se), 462.2751]. Satisfactory analytical data were not obtained for this compound. Supporting evidence for the structure comes from the properties of the hydrocarbon obtained (37%) by Ph_3SnH -reduction:⁸² mp $78-79^{\circ}\text{C}$; $[\alpha]_D^{25} +72.5^{\circ}$ (c 1.18, CHCl_3), NMR (CDCl_3) δ inter alia 0.68 (s); 1.0 (s). Cholest-4-ene has^{162a} mp values in the range $77-83^{\circ}\text{C}$; $[\alpha]_D^{25} +71 \pm 5^{\circ}$ ^{162a} (c 1-5, CHCl_3); NMR (CDCl_3) δ inter alia 0.67 (s); 0.99 (s).^{162b}

1,1,1-Tris(methylseleno)ethane (entry 10, Table VII)

Tris(methylseleno)borane (32) (546 mg, 1.87 mmol) and then TFA (10 μL , 0.130 mmol) were injected into a stirred solution of 1,1,1-trimethoxyethane (209 mg, 1.74 mmol) in CHCl_3 (5 mL). After 13 h the solvent was evaporated. Chromatography of the residue over alumina (3 x 50 cm) with hexane gave 213 mg (39%) of the major product as a homogeneous (TLC, alumina, hexane) oil; NMR (CDCl_3) δ 2.1 (s, 9H), 2,23 (s, 3H); m/e 311.8451 [calcd for $\text{C}_5\text{H}_{12}^{80}\text{Se}_3$, 311.8435]. For analysis the material was distilled in a Kugelrohr: bp 110° (20 mm).

Anal. Calcd for $C_5H_{12}Se_3$: C, 19.43; H, 3.91. Found: C, 19.61; H, 3.73.

1-Methoxy-1-(phenylseleno)undecane (entry 1, Table VIII)

The acetal¹⁵² (515 mg, 2.38 mmol) was added from a syringe over 2 min to a magnetically stirred mixture of tris(phenylseleno)borane (416 mg, 0.87 mmol) and toluene (2 mL). After 6 h the solution was diluted with MeOH (3 mL) and $NaBH_4$ was added in portions to give a colorless solution which was partitioned between pentane (200 mL) and water (100 mL). The pentane layer was washed with water (3 x 100 mL), dried (Na_2SO_4), filtered, and evaporated to leave 714 mg (87%) of the mixed acetal as a pale yellow oil; NMR ($CDCl_3$) δ 0.75-2.05 (m, 21H), 3.41 (s, 3H), 4.89 (t, 1H, $J = 6.1$ Hz), 7.25 and 7.6 (m, 5H); m/e 342.1458 [calcd for $C_{18}H_{30}O^{80}Se$, 342.1462]. Anal. Calcd for $C_{18}H_{30}OSe$: C, 63.33; H, 8.86; O, 4.69. Found: C, 63.11; H, 8.88; O, 4.82.

1-[Methoxy(phenylseleno)methyl]naphthalene (entry 2, Table VIII)

A magnetically stirred mixture of tris(phenylseleno)borane (540 mg, 1.13 mmol) in $CHCl_3$ (5 mL) was cooled in a bath kept at $-30^\circ C$. The acetal¹⁵⁶ (681 mg, 3.37 mmol) was added from a syringe over 1 min. After 15 min the cooling bath was removed and stirring was

continued for 7.5 h. The solvent was evaporated, the residue was stirred with MeOH (6 mL), and NaBH_4 was added in small portions until a colorless methanol solution (covering a pale yellow oil) was obtained. The mixture was partitioned between pentane (200 mL) and water (100 mL). The aqueous layer was washed with pentane (100 mL) and the combined pentane layers were washed with water (4 x 100 mL) and dried (Na_2SO_4). Filtration, evaporation of the solvent and crystallization of the residue from hexane (3 mL) gave 860 mg (78%) of the mixed acetal as pale yellow crystals; mp 60-63°C; NMR (CDCl_3) δ 3.6 (s, 3H), 6.55 (s, 1H), 7.0-8.25 (m, 12H); m/e 328.0361 [calcd for $\text{C}_{18}\text{H}_{16}\text{O}^{80}\text{Se}$, 328.0367]. Anal. Calcd for $\text{C}_{18}\text{H}_{16}\text{OSe}$: C, 66.06; H, 4.93; O, 4.89. Found: C, 66.12; H, 4.97; O, 4.89.

5-Methoxy-5-(phenylseleno)nonane (entry 3, Table VIII)

With the differences noted, this reaction was carried out as described for entry 1, Table VIII using the acetal¹⁵³ (390 mg, 2.07 mmol), tris(phenylseleno)-borane (351 mg, 0.73 mmol), and toluene (2 mL). After 1 h the mixture was diluted with MeOH (4 mL) and processed as described to yield 520 mg (80%) of the mixed acetal as a pale yellow liquid; NMR (CDCl_3) δ 0.75-1.9 (m, 18H), 3.42 (s, 3H), 7.25 and 7.5 (m, 5H); m/e

157.1589 [calcd for $C_{10}H_{61}O$ (M-PhSe), 157.1592]. Anal.

Calcd for $C_{16}H_{26}OSe$: C, 61.33; H, 8.36; O, 5.11. Found:
C, 61.45; H, 8.59; O, 5.43.

Deoxygenation of Epoxides

Se-Methyl-O,O-diethyl phosphoroselenoate (73)

Sodium salt⁵⁹ (17) (0.9464 g, 3.96 mmol) was dissolved in dry THF (20 mL), and to this solution was added CH_3I (0.5840 g, 4.12 mmol) in dry THF (5 mL) in one portion via syringe. The solution was stirred 1 h at room temperature, refluxed 0.5 h, and the solvent evaporated. The oily residue was taken into CH_2Cl_2 (100 mL), washed with water (100 mL), dried (Na_2SO_4), filtered and the solvent evaporated. The resulting pale yellow liquid (0.7743 g, 84.6%) was homogeneous by TLC (silica gel, ethyl acetate); NMR (CDCl_3) δ 4.22, 4.07 (overlapping q, $J = 7$ Hz, 4H), 2.16 (d, $J = 14$ Hz, 3H), 1.38 (t, $J = 7$ Hz, 6H); m/e (low resolution) 232 ($\text{C}_5\text{H}_{13}\text{O}_3\text{P}^{80}\text{Se}$).

Stock Solution of Sodium Diethyl Phosphite in Ethanol

Diethyl phosphite (14.24 g, 103 mmol) was injected over 15 min into a magnetically stirred solution of sodium (2.39 g, 104 mmol) in anhydrous ethanol (150 mL). The solution was stirred for at least 30 min prior to use and was stored under a slight static pressure of nitrogen.

Stock Solution of Lithium Diethyl Phosphite in THF

Diethyl phosphite (53.75 g, 38.92 mmol) was stirred overnight with dry THF (20 mL) and lithium (270.1 mg,

38.92 mmol, cut into small pieces). All the lithium dissolved and the solution was stored under a slight static pressure of nitrogen.

Stock Solution of Potassium Diethyl Phosphite in THF

The method used for the corresponding lithium salt was followed but with potassium (315.7 mg, 8.074 mmol) and diethyl phosphite (1.125 g, 8.146 mmol).

Preparation of (4E,8Z)-4,5,8,9-Diepoxydodecane (74)

(4E,8Z)-Dodecadiene¹²² (392.5 mg, 2.36 mmol) was dissolved in dichloromethane (50 mL) and the solution was cooled in an ice bath. m-Chloroperbenzoic acid (982.2 mg, equivalent to 4.83 mmol) in dichloromethane (20 mL) was added over 20 min with stirring. The temperature was kept near 0° for 2 h more and stirring was continued overnight at room temperature. The solution was washed with aqueous sodium hydroxide (50 mL, 1N) and then with water. The organic layer was dried (Na₂SO₄) and evaporated at room temperature (water pump). The colorless residue was distilled in a Kugelrohr apparatus (oven temperature 73°, 0.05 mm) to give the diepoxide (74) (406.7 mg, 86%) as a colorless, homogeneous (TLC, silica, chloroform) liquid; NMR (CDCl₃) δ 0.6-1.2 (m, 6H), 1.2-2 (m, 12H), 2.5-2.8 and 2.8-3.1 (two partially overlapping m, each 2H); ¹³C NMR (CDCl₃) δ 58.9, 58.7, 58.3, 58, 57.2, 57.1,

56.7, 56.4, 34.1, 29.8, 29.6, 29.2, 24.8, 24.4, 19.9, 19.4, 14.0; m/e 198.1618 [calcd for $C_{12}H_{22}O_2$, 198.1627].
 Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18.
 Found: C, 72.82; H, 11.28. The ^{13}C NMR confirms the expectation that the material is a mixture of the syn and anti diastereoisomers.

Comparative Reactivity of $(EtO)_2P(O)SeNa$ (17) and $(EtO)_2P(O)TeNa$ (71)

A. Reactions of $(EtO)_2P(O)SeNa$ (17) with 1,2-Epoxyoctane (eq. (83))

(a) Sodium diethyl phosphite (243.8 mg, 1.523 mmol) in ethanol (1 mL of a stock solution) was injected into a 5 mL septum-closed flask containing selenium powder (27.3 mg, 0.346 mmol). The mixture was stirred for a few minutes until all the metal had dissolved and then 1,2-epoxyoctane^{163a} (197.6 mg, 1.541 mmol) was injected. Stirring was continued for 13 h and the mixture was then examined by VPC^{163b} with the following result: (Rel. peak areas) epoxide:olefin: 12:1.

(b) With the exception noted below the above experiment was repeated using selenium (114.9 mg, 1.455 mmol), sodium diethyl phosphite (243.8 mg, 1.523 mmol) in ethanol (1 mL) and 1,2-epoxyoctane (164.1 mg, 1.280 mmol). [Prior to injection of epoxide the selenium-

sodium diethyl phosphite mixture was stirred 1.5 h. Not all the selenium dissolved.] Stirring was continued for 13 h and the mixture was then examined by VPC with the following result: (Rel. peak areas) epoxide:olefin: 7:23.

B. Reaction of $(\text{EtO})_2\text{P}(\text{O})\text{TeNa}$ with 1,2-Epoxydecane (eq. (87))

(a) Sodium diethyl phosphite (219.3 mg, 1.37 mmol) in ethanol (2 mL of a stock solution) was injected into a septum-closed flask containing tellurium powder (10 mg, 0.0784 mmol). The mixture was stirred for a few minutes until all the metal had dissolved and then 1,2-epoxydecane^{164a} (160 mg, 1.024 mmol) and octane (130.4 mg, as internal standard) were injected. The mixture remained clear and periodic analysis by VPC^{164b} showed that the epoxide was being converted into olefin. After 1.5 h a black precipitate started to form. After 7.5 h all the epoxide had reacted (VPC) and the absolute yield of olefin was 71.8%.^{164c}

(b) The experiment was repeated using stock solution (2 mL), tellurium powder (30 mg, 0.235 mmol), 1,2-epoxydecane (172.4 mg; 1.103 mmol) and octane (149.6 mg). This reaction differs from that just described only in the increased amount of tellurium. A black precipitate formed 30 min after addition of the epoxide and reaction was complete within 2 h (VPC control). The yield of

olefin (VPC) was 90.2%.

Reaction of $(\text{EtO})_2\text{P}(\text{O})\text{TeNa}$ with a Mixture of 1,2-Epoxy-
octane and 7-Oxabicyclo[4.1.0]heptane (eq. (88))

Sodium diethyl phosphite (110 mg, 0.687 mmol) in ethanol (1 mL of a stock solution) was injected into a 5 mL septum-closed flask containing tellurium powder (28.7 mg, 0.225 mmol). The mixture was stirred and after a few minutes all the metal had dissolved. 1,2-Epoxyoctane^{163a} (161.1 mg, 1.256 mmol) was then injected followed immediately by 7-oxabicyclo[4.1.1]heptane^{165a} (120 mg, 1.223 mmol) and dodecane (129.5 mg, as internal standard). Within 3 min a black precipitate formed and, after 30 min (from the time of addition of the epoxides) more sodium diethyl phosphite (55 mg, 0.344 mmol) in ethanol (0.5 mL) was injected. After a further 30 min had elapsed a black precipitate formed again and another identical portion of the stock solution of sodium diethyl phosphite was injected. Fifteen min later the mixture was examined by VPC,^{165b} the following relative peak areas being found: 1-octene (14), 1,2-epoxyoctane (7), cyclohexene (1), 7-oxabicyclo[4.1.0]heptane (14). More sodium diethyl phosphite (110 mg, 0.687 mmol) was injected in two equal portions, one at this stage and the other after 1 h, bringing the total quantity used to 330 mg (2.06 mmol). Stirring was continued 3 h beyond the last

addition and the following yields (based on the dodecane internal standard)^{165c} were measured by VPC: 1-octene (100%), 1,2-epoxyoctane (trace), cyclohexene (20%), 7-oxabicyclo[4.1.0]heptane (80%).

Deoxygenation of 1,2-Epoxyoctane. Non Stoichiometric Procedure using $(\text{EtO})_2\text{P}(\text{O})\text{TeNa}$ (entry 1, Table IX)

Tellurium powder (214.9 mg, 1.684 mmol) was placed in a 250 mL round bottomed flask containing a magnetic stirring bar and closed by a septum. The flask was flushed with nitrogen and then kept under a slight static pressure of the gas. 1,2-Epoxyoctane^{163a} (12.180 g, 95.01 mmol) was added by syringe and a stock solution of sodium O,O-diethyl phosphite [170 mL, 107.4 mmol $(\text{EtO})_2\text{P}(\text{O})\text{Na}$] was added with stirring at a uniform rate (syringe pump) over 11 h. The mixture was then stirred overnight after which it was filtered through cotton wool, diluted with water (1 L) and extracted with isopentane (3 x 300 mL). The combined organic extract was dried (Na_2SO_4) and, using a spinning band apparatus, it was concentrated and distilled. 1-Octene (7.763 g, 72%) was obtained as a colorless liquid: bp 112°. Analysis by VPC (on two different silver ion-impregnated columns)¹⁶⁶ showed that the material was better than 99% pure. [The columns were able to separate all octene isomers]. The product had identical NMR as authentic 1-octene.

Deoxygenation of 1,2-Epoxydecane. Non-stoichiometric
procedure using $(\text{EtO})_2\text{P}(\text{O})\text{TeNa}$ (entry 2, Table IX)

Tellurium powder (2.00 g, 15.67 mmol) was placed in a 100 mL round bottomed flask containing a magnetic stirring bar and closed by a septum. The flask was flushed with nitrogen and kept under a slight static pressure of the gas. 1,2-Epoxydecane^{164a} (10.00 g, 63.99 mmol) was added by syringe and a stock solution of sodium O,O-diethyl phosphite [47.0 mL, 71.6 mmol $(\text{EtO})_2\text{P}(\text{O})\text{Na}$] was added with stirring at a uniform rate (syringe pump) over 1.5 h. After a further 2 h (stirring) an additional portion of stock solution [5 mL, 7.62 mmol $(\text{EtO})_2\text{P}(\text{O})\text{Na}$] was added rapidly. Stirring was continued 8.5 h and, since epoxide was still present (VPC control)¹⁶⁷ a further portion [5 mL, 7.62 mmol $(\text{EtO})_2\text{P}(\text{O})\text{Na}$] was added rapidly. After 8 h a final addition [3 mL, 4.57 mmol $(\text{EtO})_2\text{P}(\text{O})\text{Na}$] of stock solution was made and stirring was continued for 6 h. At this stage [i.e., total reaction time of 26 h; total reagent 91.41 mmol $(\text{EtO})_2\text{P}(\text{O})\text{Na}$] the mixture was poured into water (100 mL) and extracted with dichloromethane (5 x 30 mL). The combined extracts were washed with water, dried (Na_2SO_4) and concentrated by slow distillation (1 atm) using a Vigreux column (1 x 15 cm). Spinning band distillation of the residue gave 1-decene (6.286 g,

70%) as a colorless liquid: bp 70° (water pump vacuum). The material was 99.9% pure by VPC and had identical NMR as authentic 1-decene.

Deoxygenation of 1,2-epoxyeicosane. Non-stoichiometric procedure with $(\text{EtO})_2\text{P}(\text{O})\text{TeNa}$ (entry 3, Table IX)

Tellurium powder (130 mg, 1.019 mmol) and 1,2-epoxyeicosane¹⁶⁸ (1.956 g, 6.596 mmol) were placed in a 25-mL round bottomed flask containing a magnetic stirring bar and closed by a septum. The flask was flushed with nitrogen and then kept under a slight static pressure of the gas. A stock solution of sodium O,O-diethyl phosphite [110 mg $(\text{EtO})_2\text{P}(\text{O})\text{Na}$ per mL] was injected in portions in the following manner. Each injection caused the tellurium to dissolve; the next injection was not made until the metal had precipitated. The portions and addition times of the stock solution were 5.00 mL (0 min), 5.00 mL (20 min), 2.00 mL (85 min), 2.00 mL (115 min), i.e., 16.00 mL containing 1.760 g (10.994 mmol) sodium O,O-diethyl phosphite were added over ca. 2 h. The mixture was stirred overnight, the tellurium was removed by filtration through a plug of cottonwool and the filtrate was partitioned between dichloromethane (50 mL) and water (50 mL). The aqueous layer was washed with dichloro-

methane (50 mL) and the combined organic extracts were dried (Na_2SO_4) and evaporated. The residue was chromatographed over neutral Brockman activity I alumina (3 x 18 cm) with pentane to afford eicosene (1.697 g, 91%) as a colorless liquid that crystallized on standing. The material was homogeneous by TLC (silica impregnated with 15% silver nitrate, benzene) and was identified by spectroscopic comparison (NMR and MS) with an authentic sample of eicosene.

Reaction of $(\text{EtO})_2\text{P}(\text{O})\text{TeNa}$ with (E)-4,5-Epoxyoctane
(entry 4, Table IX)

Sodium O,O-diethyl phosphite (219.9 mg, 1.37 mmol) in ethanol (2 mL of a stock solution) was injected into a septum-closed flask containing tellurium powder (28.8 mg, 0.226 mmol) and the mixture was stirred magnetically until all the metal had dissolved. (E)-4,5-Epoxyoctane^{169a} (152.6 mg, 1.19 mmol) was added by syringe followed by dodecane (172.4 mg, as internal standard). After 13 h at room temperature analysis by VPC^{169b} showed that the absolute yield^{169c} of oct-4-ene was < 1% and that > 97% of the epoxide remained.

Selective deoxygenation of 1,2,8,9-diepoxy-p-menthane.

Non-stoichiometric procedure using $(\text{EtO})_2\text{P}(\text{O})\text{TeNa}$ (entry 5, Table IX).

Tellurium powder (12.1 mg, 0.095 mmol) was placed in a 10 mL round bottomed flask equipped with a magnetic stirring bar and closed by a rubber septum. The flask was purged with nitrogen and kept under a slight static pressure of the gas. 1,2,8,9-Diepoxy-p-menthane^{170a} (255.1 mg, 1.516 mmol) and dodecane (122.2 mg, internal standard) were injected followed by sodium O,O-diethyl phosphite (487.6 mg, 3.046 mmol) in ethanol (2 mL of a stock solution). The phosphite solution was added in 0.20 mL portions over 17 h, each portion being added only when tellurium had precipitated after the previous addition. The time needed for the black precipitate to appear changed from 20 min (after the first addition) to 7 h (after the last addition). The mixture was stirred 1.5 h after the final appearance of the tellurium deposit and analysis of the solution by VPC^{170b} showed that the absolute yield^{170c} of 1,2-epoxy-p-menth-8-ene^{170a} was 76%. A portion was isolated and its NMR spectrum was identical to an authentic sample.

Deoxygenation of 7-oxabicyclo[4.2.1]heptane. Non-stoichiometric procedure using $(\text{EtO})_2\text{P}(\text{O})\text{TeNa}$ (entry 6, Table IX)

Sodium O,O-diethyl phosphite (219.9 mg, 1.374 mmol) in ethanol (2 mL of a stock solution) was injected into a septum-closed flask containing tellurium powder (35.3 mg, 0.277 mmol) and the mixture was stirred magnetically until all the metal had dissolved. 7-Oxabicyclo[4.2.1]heptane (119.5 mg, 1.218 mmol) was added by syringe followed by dodecane (153.7 mg). The progress of the reaction was monitored by VPC^{171a} and after 42 h of stirring at room temperature no epoxide remained. The absolute yield^{171b} of cyclohexene was 88.6%.

General method for preparation of O,O-diethyl phosphorotelluroates (71)

The apparatus consisted of a 5-mL round bottomed flask fused onto the end of a small condenser which carried a straight vacuum takeoff. Tellurium powder and a small magnetic stirring bar were placed in the flask. The apparatus was assembled and evacuated to 0.05 mm. The tap of the vacuum takeoff was closed and the tip of the hose connector portion was capped with a septum. The space between the tap and the septum was flushed with nitrogen, and nitrogen was then allowed to leak slowly

into the flask. The appropriate O,O-diethyl phosphite in THF (from a stock solution) was injected into the vessel followed, sometimes, by a small volume of pure, dry THF. The mixture was stirred (under nitrogen) until all the tellurium had dissolved (1 to 2 h). The solvent was evaporated at room temperature through the vacuum takeoff (using an oil pump) to leave a white residue. The vacuum takeoff was capped with a septum and, by the same procedure as before, nitrogen was introduced into the flask. Anhydrous ethanol was injected to afford a colorless, and usually clear, solution.

Comparison of the reactivity of potassium, sodium and lithium O,O-diethyl phosphorotelluroates (71)

A. Reaction of $(\text{EtO})_2\text{P}(\text{O})\text{TeK}$ with (Z)-4,5-Epoxyoctane

Solid potassium O,O-diethyl phosphorotelluroate was prepared by the special technique described above from tellurium powder (31 mg, 0.243 mmol), potassium O,O-diethyl phosphite (59.3 mg, 0.337 mmol) in THF (0.25 mL of a stock solution) and a portion (1 mL) of dry THF. The solid residue was stirred with anhydrous ethanol (1.5 mL) to give a clear and colorless solution. (Z)-4,5-Epoxyoctane^{169a} (37.1 mg, 0.289 mmol) was introduced

by syringe and the mixture was stirred (nitrogen atmosphere) for 22 h. At this stage a tellurium mirror had been deposited and analysis of the reaction mixture by VPC¹⁷² showed the following relative mole ratios: olefin (1), epoxide (3). The mixture was refluxed for 7.5 h and VPC analysis then showed new relative mole ratios: olefin (5), epoxide (3).

B. Reaction of $(\text{EtO})_2\text{P}(\text{O})\text{TeNa}$ with (Z)-4,5-Epoxyoctane

Tellurium powder (175.7 mg, 1.38 mmol) was added to a stirred solution of sodium diethyl phosphite [from diethyl phosphite (308.9 mg, 2.24 mmol), sodium (51.6 mg, 2.24 mmol) and dry ethanol (3 mL)]. After 2 h all but a trace of tellurium had dissolved and (Z)-4,5-epoxyoctane (260 mg, 2.03 mmol) was injected. After 12 h at room temperature analysis of the reaction mixture by VPC¹⁷² showed the following relative mole ratio: epoxide:olefin: 5.29:1. After 24 h the ratio was 3.2:1.

C. Reaction of $(\text{EtO})_2\text{P}(\text{O})\text{TeLi}$ with (Z)-4,5-Epoxyoctane

Solid lithium O,O-diethyl phosphorotelluroate was prepared in the usual way from tellurium powder (68.1 mg, 0.53 mmol) and lithium O,O-diethyl phosphite (140.1 mg, 0.973 mmol) in THF (1 mL of a stock solution). The reagent

was stirred with anhydrous ethanol (1.5 mL) and (Z)-4,5-epoxyoctane (108 mg, 0.842 mmol) was added. After 12 h at room temperature analysis of the reaction mixture by VPC¹⁷² showed the following relative mole ratios: epoxide:olefin: 0.95:1.

Stereochemistry of the Deoxygenation

A. Reaction of (EtO)₂P(O)TeLi with (Z)-4,5-epoxyoctane (entry 7, Table IX)

The previous experiment was repeated using tellurium powder (363.2 mg, 2.846 mmol) and lithium O,O-diethyl phosphite (419.9 mg, 2.915 mmol) in THF (1 mL of a stock solution). The solid tellurium reagent was stirred with anhydrous ethanol (2 mL) and (Z)-4,5-epoxyoctane^{169a,173a} (359.9 mg, 2.807 mmol) was added. The mixture was then refluxed for 2 h and partitioned between hexane (20 mL) and water (10 mL). The hexane layer was washed three times with water (3 x 10 mL) and was then dried (MgSO₄). Dodecane (311.6 mg) was added to the solution as an internal standard and VPC^{173b} analysis showed the absolute yields^{173c} of olefin and epoxide to be 76.7% and 16.5%, respectively. Analysis by VPC on a silver nitrate-impregnated column^{166a} showed that the ratio of (Z) to (E)-oct-4-ene was 56:1.

B. Reaction of $(\text{EtO})_2\text{P}(\text{O})\text{TeLi}$ with (E)-4,5-Epoxyoctane (entry 8, Table IX)

The previous experiment was repeated using tellurium powder (315.5 mg, 2.47 mmol) and lithium O,O-diethyl phosphite (419.9 mg, 2.92 mmol) in THF (1 mL of a stock solution). The solid tellurium reagent was stirred with anhydrous ethanol (2 mL) and (E)-4,5-epoxyoctane^{169a,174a} (362.5 mg, 2.83 mmol) was added. The mixture was refluxed for 19 h and it was then partitioned between hexane (20 mL) and water (10 mL). The hexane layer was washed with water (5 x 8 mL), dried (MgSO_4), and analyzed by VPC using a silver nitrate-impregnated column.^{166a} The mole ratio of (E):(Z) olefin was 62:1. Dodecane (308.1 mg, as an internal standard) was added to the hexane solution and VPC^{173b} analysis showed that the yield^{174b} of olefin was 46.6% and the recovery of epoxide 27.9%.

Reaction of $(\text{EtO})_2\text{P}(\text{O})\text{TeLi}$ with a mixture of (Z)- and (E)-4,5-epoxyoctane (eq. (89))

Solid lithium O,O-diethyl phosphorotelluroate was prepared as described above from tellurium powder (520 mg, 4.075 mmol) and lithium O,O-diethyl phosphite (629.9 mg, 4.373) in THF (1.5 mL of a stock solution). The salt was dissolved in anhydrous ethanol (2 mL).

(Z)-4,5-Epoxyoctane (327 mg, 2.550 mmol) and then the (E)-isomer (315 mg, 2.457 mmol) were injected into the reaction vessel. The mixture was refluxed for 1 h and then partitioned between hexane (20 mL) and water (30 mL). The hexane layer was washed with water (5 x 10 mL) and dried (Na_2SO_4). Dodecane (391.3 mg) was added as an internal standard and the mixture was analyzed by VPC using ordinary^{173b} and silver nitrate-impregnated^{166a} columns. The absolute yield/recoveries were as follows: (E)-4,5-epoxyoctane (72.2%), (Z)-4,5-epoxyoctane (12.4%), (Z)-oct-4-ene (80.6%), (E)-oct-4-ene (25.2%).

Selective Deoxygenation of (4E,8Z)-4,5,8,9-diepoxydodecane (74). Stoichiometric procedure with $(\text{EtO})_2\text{P}(\text{O})\text{TeLi}$ (entry 9, Table IX)

Lithium O,O-diethyl phosphorotelluroate was prepared by the general procedure described above from tellurium powder (588.1 mg, 4.609 mmol) and lithium O,O-diethyl phosphite (627 mg, 4.353 mmol) in THF (2.25 mL of a stock solution), the mixture being diluted with dry THF (5 mL). The crystalline reagent was generated in the usual way and then dissolved in dry ethanol (5 mL). (4E,8Z)-4,5,8,9-Diepoxydodecane (733.5 mg, 4.023 mmol) was placed in a 10 mL round bottomed flask closed with a

septum. The flask was purged with nitrogen and kept under a slight static pressure of the gas. By using a syringe the solution of tellurium reagent (3 mL) was added, with magnetic stirring, to the diepoxide. After 12 h a further portion of the solution (1 mL) was added and, after 3 h, the remainder of the tellurium reagent solution was injected, using dry ethanol (2 x 1 mL) as a rinse. The reaction mixture was stirred 2 h more and was then partitioned between pentane (50 mL) and the combined organic extracts were dried (Na_2SO_4) and evaporated at room temperature (water pump). The residue was chromatographed over silica gel (1.5 x 40 cm) with chloroform to afford two fractions. The less polar was a colorless oil which, after Kugelrohr distillation, weighed 40.9 mg (6.6%). Its NMR and IR spectra were identical to those of (4E,8Z)-4,8-dodecadiene.¹²² The second fraction was distilled (Kugelrohr, oven temperature 62°, 0.15 mm) to afford monoepoxide (357 mg, 52.94%) as a colorless liquid. Examination by TLC (silica, 5% AgNO_3 , chloroform) showed a large spot (jet black with hot sulfuric acid) at $R_f \sim 0.5$ and a faint spot (dark with hot sulfuric) at $R_f \sim 0.55$. Bisepoxide was absent. The material had NMR (CDCl_3 , 400 MHz) δ 0.91 (t, $J = 7.4$ Hz, 3H), 0.96 (t, $J = 4$ Hz, 3H), 1.3-1.7 (m, 8H, incorporating q, $J = 7.3$ Hz, 2H), 2.01 (q, $J = 6.8$ Hz, 2H), 2.19 (q, $J = 6.8$ Hz, 2H), 2.68 (approx. t, $J = 4.9$ Hz, 2H), 5.3-5.5 (m, 2H). [A weak

multiplet centred at 2.92 δ indicated (by comparison with signal at 2.68 δ) that 10.8% of (4Z,8E)-4,5-epoxydodec-8-ene was present. NMR spectra (CDCl_3) on authentic (Z) and (E)-4,5-epoxyoctanes showed the vinyl multiplets at 2.8 and 2.65 δ , respectively]. ^{13}C NMR (CDCl_3) δ 130.6, 128.6, 58.7, 58.3, 34.2, 32.4, 29.3, 23.9, 22.8, 19.4, 14.0, 13.8. The ^{13}C NMR spectrum showed weak signals at 131.2, 129.2, 57.0, 56.6, 34.7, 30.0, 29.7, 28.1, 22.7, 20.0. m/e 182.1671 [calcd for $\text{C}_{12}\text{H}_{22}\text{O}$, 182.1669]. Anal. Calcd for $\text{C}_{12}\text{H}_{22}\text{O}$: C, 79.06; H, 12.16. Found: C, 79.37; H, 12.14.

Deoxygenation of 2 β ,3 β -oxido-5 α -cholestane. Stoichiometric procedure using $(\text{EtO})_2\text{P}(\text{O})\text{TeLi}$ (entry 10, Table IX).

Lithium O,O-diethyl phosphorotelluroate was prepared by the general procedure described above from tellurium powder (33.0 mg, 0.259 mmol) and lithium O,O-diethyl phosphite (41.9 mg, 0.29 mmol) in THF (0.15 mL of a stock solution), the mixture being diluted with dry THF (1 mL). The crystalline reagent was generated in the usual way and then dissolved in dry ethanol (0.2 mL). Another unit of the special apparatus used to generate the tellurium reagent was charged with 2 β , 3 β -oxido-5 α -cholestane¹⁷⁵ (100.0 mg, 0.259 mmol) and filled with nitrogen by the special technique described above for use with such

apparatus. By means of a syringe, the ethanol solution of the tellurium reagent was injected, with magnetic stirring, into the reaction vessel, further portions (3 x 0.2 mL) of ethanol being used as a rinse. [This protocol was adopted because the steroid is insoluble in ethanol, which is a good reaction solvent.] The reaction mixture was refluxed for 5.5 h and the black mixture was partitioned between ether (50 mL) and water (50 mL). The ether layer was washed with water (2 x 10 mL), once with saturated aqueous sodium chloride solution and it was then dried (MgSO_4). Evaporation and chromatography of the residue over silica gel (2.5 x 10 cm) with toluene gave 5 α -cholest-2-ene (86.4 mg, 90%); mp 73-75°; $[\alpha]_D = 66.7^\circ$ ($c = 2.745$, CHCl_3).^{175b} The material was homogeneous by TLC (silica impregnated with 5% AgNO_3 ; 2:98 benzene-hexane). The ^{13}C MR spectrum showed a one to one correspondence with the published data.^{175c}

Deoxygenation of 16 α ,17 α -epoxy-3-methoxyestra-1,3,5(10)-triene. Stoichiometric procedure with $(\text{EtO})_2\text{P}(\text{O})\text{TeLi}$, (entry 11, Table IX)

The tellurium reagent was generated in the usual way, but in the presence of 16 α ,17 α -epoxy-3-methoxyestra-1,3,5(10)-triene¹⁷⁶ (169.5 mg, 0.60 mmol), from tellurium (201 mg, 1.58 mmol) and lithium O,O-diethyl phosphite

(275 mg, 1.91 mmol) in THF (2 mL of a stock solution). The solid reagent, admixed with the epoxide, was stirred with dry ethanol (1.5 mL) and the mixture was refluxed for 46 h. It was then applied (without removal of solvent) to a column of silica gel (2.5 x 20 cm). Development with 1:1 hexane-benzene gave 62.8 mg (39%) of 3-methoxy-estra-1,3,5(10),16-tetraene as a homogeneous (TLC, silica, 1:1 hexane-benzene) solid; mp 65-68°; $[\alpha]_D 108^\circ$ (c 2.38, CHCl_3) [lit.¹⁷⁶ mp 66-68°; $[\alpha]_D +109^\circ$]. The NMR was identical with that of an authentic sample of the tetraene.

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144. OV-17 column, 170°; a solution of di-*t*-butyl sulfoxide and diphenyl diselenide in CHCl_3 showed no di-*t*-butyl sulfide on the VPC trace when injected under the same conditions as the VPC analysis.
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146. All of these reactions were performed under a dry nitrogen atmosphere.
147. The product from entry 3, Table V had identical IR and NMR to the product from entry 2, Table VI.
148. The product from entry 4, Table V had identical IR and NMR to the product from entry 1, Table VI.
149. No increase in yield was achieved by extending the reaction time to 24 h.
150. a) In a similar experiment carried out overnight the yield was 50%; b) The product from entry 7, Table V had identical IR and NMR to the product from entry 3, Table VI.
151. a) No significant improvement was observed by extending the reaction time to 14 h; b) The product from entry 8, Table V had identical IR and NMR to the product from entry 4, Table VI.
152. This compound was prepared from undecanal (6.0 g, 35.2 mmol) trimethyl orthoformate (7.0 g, 66.0 mmol) and H_2SO_4 (2 drops) in dry (distilled from Mg) methanol (50 mL) stirred for 2 days at room temperature. Addition of 1 mL triethylamine followed by distillation yielded a colorless liquid, bp 105-108° (3 mm) (J. W. Farquhar, J. Lipid. Research, 1962, 3, 21); NMR (CDCl_3) δ 4.30 (t, $J = 5 \text{ Hz}$, 1H), 3.23 (s, 6H), 1.7-0.7 (21H).

153. 5,5-Dimethoxynonane was prepared exactly as in ref. 152 yielding a colorless liquid, bp 74-76° (4 mm); NMR (CDCl₃) δ 3.11 (s, 6H), 1.7-0.7 (18H). Anal. Calcd for C₁₁H₂₄O₂: C, 70.16; H, 12.85. Found: C, 70.33; H, 12.81.
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156. 1-(Dimethoxymethyl)naphthalene was prepared exactly as in ref. 152 yielding a colorless liquid, bp 103-108° (0.01 mm): NMR (CDCl₃) δ 8.4-8.2 (m, 1H), 7.9-7.2 (m, 6H), 5.85 (s, 1H), 3.30 (s, 6H) (D. M. Baily, Chem. Abs., 1973, 78, 14767n).
157. This product was isolated and characterized by NMR and MS in another identical experiment.
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b) OV-1 column, 110°.

164. a) This compound was prepared from 1-decene and 85% m-chloroperbenzoic acid in exactly the same manner as the preparation of (74): (B. Rotstein, Bull. Soc. Chim. Fr., 1935, 2, 1936); b) OV-1 column, 120°; c) The reaction mixture was compared to a standard solution composed of octane (0.1463 g), epoxide (0.1319 g), and oelfin (0.1256 g) in ethanol (2 mL).
165. a) Purchased from Aldrich; b) OV-1 column; c) The standard solutions were composed of: dodecane (0.1504 g), 1,2-epoxycyclohexane (0.1976 g), and cyclohexene (0.1327 g); and dodecane (0.1510 g), 1,2-epoxyoctane (0.1510 g), and 1-octene (0.1335 g). Both solutions were diluted with ethanol (1.5 mL).
166. a) A silver nitrate-impregnated column was prepared as follows: silver nitrate (40 g) was dissolved in ethylene glycol (40 g) and a portion (20 g) of the solution was distributed over Chromosorb P (Acid Washed 60-80 mesh) (40 g). The packing was used to fill a stainless steel column (20 ft x 1/8" O.D.). Use of test mixtures showed that this column could separate cleanly the (Z) and (E)-isomers of 4-octene and could also resolve most of the other octene isomers. The column was used at temperatures in the range 60-80°C (E. Gil-Av, J. Herling, J. Shabtai, J. Chromatog., 1958, 1, 508; E. Bendel, B. Fell, W. Gartzzen, G. Kruse, ibid., 1967, 31, 531). b) A silver tetrafluoroborate impregnated column was made as follows: silver tetrafluoroborate (3 g) was dissolved in 3,3'-oxydipropionitrile (20 g) and a portion (12 g) of the solution was distributed over Chromosorb P (Acid Washed, 60-80 mesh) (13 g). The packing was used to fill a stainless steel column (40 ft x 1/8" O.D.).
167. OV-1 column, 155°.
168. 1,2-Epoxyeicosane was prepared exactly according to the procedure for the preparation of (74) from eicosene (20.38 g, 72.6 mmol) in CH₂Cl₂ (500 mL) and m-chloroperbenzoic acid (14.63 g, 71.9 mmol) in CH₂Cl₂ (200 mL). After work-up, the product was purified by chromatography on alumina (pentane elution) yielding a white solid; mp 39.5-42; NMR (CDCl₃) δ: 3.0-2.3 (m, 3H), 1.7-0.7 (37H); m/e (low resolution): 296 (C₂₀H₄₀O).

169. a) D. E. Bissing and A. J. Speziale, J. Am. Chem. Soc., 1965, 87, 2683; b) OV-1 column, 125°; c) The reaction was compared to a standard solution composed of dodecane (0.1279 g), (E)-4,5-epoxyoctane (0.1529 g), and (E)-4-octene (0.0908 g), dissolved in ethanol (1.5 mL).
170. a) W. K. Anderson and T. Veysoglu, J. Org. Chem., 1973, 38, 2267; b) OV-1 column, 185°; c) The reaction was compared to a standard solution composed of 1,2-epoxy-p-menth-8-ene (0.0907 g) and dodecane (0.1066 g) in ethanol (2 mL).
171. a) Carbowax column, 80°; b) This reaction was compared to the standard solution in ref. 165c.
172. Carbowax column, 110°.
173. a) This compound was prepared from commercial (Z)-4-octene that contained ca. 3% of the (E)-isomer by VPC^{166a}; b) OV-1 column, 120°; c) This solution was compared to a standard solution composed of (Z)-4-octene (0.2577 g), (Z)-4,5-epoxyoctane (0.0937 g), and dodecane (0.3184 g), dissolved in hexane (20 mL).
174. a) This compound was prepared from commercial (E)-4-octene that contained ca. 1% of (Z)-isomer by VPC^{166a}; b) This solution was compared to a standard solution composed of (E)-4-octene (0.2777 g), (E)-4,5-epoxyoctane (0.1740 g), and dodecane (0.3086 g), dissolved in hexane (20 mL).
175. a) E. J. Corey, J. Am. Chem. Soc., 1953, 75, 4832; b) Reported values for mp are 66-75°; for $[\alpha]_D$, $66 \pm 2^\circ$ ^{162a}; c) J. W. Blunt and J. B. Stothers, Org. Mag. Resonance, 1977, 9, 439.
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